THE MULTISTATE ATMOSPHERIC POWER PRODUCTION

POLLUTION STUDY - MAP3S

Progress Report for FY 1977 and FY 1978

Coordinated by

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The Multi-state Atmospheric Power Production Pollution Study (MAP3S) was initiated in mid-1976 by predecessors of the present Office of Health and Environmental Research, Assistant Secretary for Environment. Their intent has been to improve understanding about the transport, transformation, and fate of pollutants released by energy-related activities. During 1976 and 1977 a formal program plan was prepared describing the rationale and direction of the planned research. This program plan and an appendix containing brief descriptions of research activities underway in FY-1977 were published in January 1978. Beginning with FY-1979, executive management of MAP3S has been vested in a joint committee from EPA[*] and DOE, with funding coming both from funds transferred to the EPA budget and from funding remaining within DOE.

This progress report has been prepared to summarize the research activities during FY-1977 and 1978, the first two years of what is envisioned as a multi-year program. This report relates these research accomplishments to the objectives set out in the program plan and to the overall research progress in each area. As a progress report, this report is not intended to be a critical review of the overall status of scientific understanding although it should serve as a basis for general progress. Rather, the report discusses specific contributions to scientific understanding made as a result of the MAP3S program, many of which have advanced the state of particular aspects of their scientific area.

The report has been prepared as a series of coordinated task descriptions by the scientists carrying out the research, with reference made to the activities of other scientists and programs. As such, some of the opinions expressed in the individual sections represent those of the author and not of everyone within MAP3S. Authors of each section are listed in the Table of Contents. A complete list of project participants by organization is included as Appendix B.

The research descriptions are intended to be semi-technical in format with references to more detailed descriptions provided. In addition, an annotated bibliography of research results from MAP3S is included in Appendix C.

It has been the dedicated efforts of the many MAP3S researchers that have provided the basis for the progress that has been made. Their efforts, both within MAP3S and in cooperation with researchers in other programs, has helped in developing a much fuller understanding of the

States. While there are still many questions remaining, they have become more tightly focused and the paths to follow to assure continued progress now appear more clear.

With much of the MAP3S program now becoming formally related to the Environmental Protection Agency, we envision even further cooperation between MAP3S and EPA's STATE, VISTTA and acid deposition programs. Together, these broad based research efforts should speed progress in addressing questions that will provide the basis for potential multi-billion dollar policy decisions relating to how best to limit health and ecological effects by controlling emissions of energy-related pollutants.

A special acknowledgement is due to Mrs. Floy Weichel, who rapidly transformed the disparate, well-marked up contributions from many organizations into a cohesive, legible document.

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set as its goal the improvement of the nation's capability to simulate the atmospheric effects of emissions from fossil-fuel powered electric generation plants. The area of study is the high-population, energy-intensive, northeastern quadrant of the United States.[*] During the first three years, the emphasis was to be on improving the understanding of the transport and fate of sulfur compounds, particularly sulfate particulate matter, because of concern over health and the potential impacts of acid deposition.

To accomplish the study's objectives, MAP3S developed a three pronged research program including ten specific tasks. Selection of the research activities recognized the need both to reduce the major uncertainties remaining in understanding the sulfur budget and to coordinate MAP3S activities with projects being supported in the complementary research programs of the Environmental Protection Agency and Electric Power Research Institute.

Since 1976, significant progress has been made to meet the MAP3S objectives through research efforts within both MAP3S and coordinated programs, in many cases through joint field experiments. This report describes the progress achieved by MAP3S researchers and attempts to place it in the context of current scientific understanding. Finally, the report lays the framework for future research. We have come a considerable way, but uncertainties remain, some now more important than previously recognized.

1.1 REGIONAL CHARACTERIZATION

The basis for better understanding of the budget of energy-related emissions is a better description of the present environment: the extent of pollutant emissions and the distribution, character and concentration of pollutants. The following points are highlights of Tasks 1 to 4 described in Chapters 3 through 6.

- Careful compiling and checking of available emissions data together with data soon to be available from the EPRI/SURE survey of power plant emissions for particular intensive measurement periods, has allowed assembly of the most

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[*]This region, referred to as the Greater Northeast, includes the upper Midwest, the Northeast, and areas directly influencing air quality in these regions.

- Data from a new sampling probe to measure stack emissions allow the first accurate characterization of concentrations of sulfuric acid (0 to 4% of sulfur in the fuel, depending on amount of excess oxygen) and metal sulfate (0.2 to 1.5% of sulfur in the fuel, depending on oxygen level and emission controls) and the correlation of emissions with plant operating characteristics.

- Development of a new instrument that provides real-time measurement of sulfuric acid and sulfate aerosol will permit much more detailed understanding of spatial and temporal variations in the next few years.

- Identification of the more toxic sulfite (S-IV) compounds in smelter plumes and urban aerosol poses new questions in characterizing regional air quality and emphasizes the need for speciation of sulfur compounds existent in ambient air.

- Careful collection and analysis of precipitation samples has shown that dissolved sulfur dioxide is an important fraction of scavenged sulfur oxides, particularly during the winter.

- Surface measurements of aerosol acidity indicate the aerosol varies from near neutral in the midwest to highly acidic in the central portion of the MAP3S region and along the east coast.

- Aircraft measurements indicate that sulfate can be transported long distances in layers above near-surface inversions.

- Current deposition of sulfur (8-15 kg/ha/yr) in the eastern United States is large relative to estimates of the natural deposition rate (< 1 kg/ha/yr).

- MAP3S network results show that sulfate concentrations in precipitation have a summer maximum, although wintertime concentrations are also substantial. Monthly average sulfate concentrations are remarkably constant over the eastern United States and the pH of rainfall is near 4.0.

- The concentration of nitrate in precipitation is relatively constant over the year, with the maximum relative concentration in winter when it may contribute (on the average) up to half of the acidity.

influence on acid deposition.

- There has been a decrease in pH in the midwestern and southern United States over the last twenty years, but this may in part be due to a decrease in the soil component in the collected rain.

- Continued and expanded monitoring of precipitation chemistry is required to better evaluate trends, mechanisms, and ultimately to provide the data base for assessment of effects.

- Collecting precipitation on an event basis is essential if the sources of the pollutants are to be identified through trajectory analyses.

1.2 FIELD EXPERIMENTS

The MAP3S program is conducting focused field experiments to allow investigation of the role of particular processes in transporting, transforming and removing sulfur compounds. Further, we have initiated a limited, preliminary evaluation of the impact that small aerosol particles (most of which are sulfate) may have in modifying the visibility and on the extent and amount of precipitation. Based on these experiments, better representations of these processes are being formulated to allow inclusion in comprehensive regional models. The following findings are highlights of Tasks 5 to 9 described in Chapters 7 through 11.

- Observations of the structure of the planetary boundary layer in the AMBIENS field experiment helped improve the description of the diurnal cycle that mixes pollutants vertically during the day and isolates them from the surface at night.

- The DACSE-I field experiment confirmed the hypothesis of long distance transport of sulfate aloft along isentropic surfaces (i.e., levels of constant potential temperature).

- Development of new inert tracers, and testing out to distances of 100 km has laid the foundation for future studies to follow air masses out to distances of 500 km and more.

- A new objective analysis algorithm allows adjustment of observed wind and vertical structure information to ensure conservation of mass and energy, thereby improving the

diurnal cycle.

- Laboratory and field studies of ^{18}O appear to indicate t[
  aqueous conversion of SO_2 to sulfate may be more import[
  than direct scavenging of sulfates in contributing to precipita[
  sulfur.

- Power plant plume sampling and analysis of results sl[
  conversion of SO_2 to sulfate is relatively slow (< 1%/hr), exc[
  during mid-day conditions when outside air is mixed with [
  plume (up to 3%/hr). A growing consensus supporting s[
  relatively limited conversion is emerging from the vari[
  diverse opinions of several years ago.

- Measurements of particle emissions from smelters indicate t[
  significant (from 10 to 40% of total plume particulate sul[
  concentrations of reduced sulfur (S-IV) can result downwind [
  the source from absorption of SO_2 by ambient aerosols.

- Studies in plumes from urban areas indicate that [
  transformation can be significantly higher than in power pl[
  plumes when the general level of photochemical activity is l[
  and necessary precursor pollutants are present (on the order [
  5%/hr).

- Preliminary results from the AMBIENS field study indicate t[
  transformation of SO_2 to $SO_4^=$ continues to occur in polluted [
  masses well away from source regions.

- Numerical modeling studies of smog chamber data have allo[
  formulation of a condensed reaction set suitable for use [
  modeling homogeneous transformation processes on a regi[
  scale.

- Field measurements have shown that the surface removal [
  small particles (mainly sulfates) is a function of surface [
  atmospheric conditions, but, although quite variable, is on [
  average more rapid than had been generally believed. S[
  particle deposition velocities were found to reach 1.0 cm/[
  with daily averages of about 0.5 cm/sec. SO_2 deposi[
  velocities were found to have very similar values.

- A numerical formulation of the dry deposition process will al[
  diurnally, seasonally and spatially dependent calculation of [
  important removal mechanism.

a physically realistic scavenging parameterization.

- Continued analysis of METROMEX data has indicated that precipitation appears to be modified by urban areas and/or the pollutant emissions from such areas, raising the prospect that such impacts may also occur on larger scales.

1.3 NUMERICAL MODELING AND ANALYSIS

Ultimately, being able to accurately simulate and assess the atmospheric effects of altered emissions patterns is the capability needed for policy evaluation. When MAP3S began, models were just becoming available that treated the regional problem with simplified, often only statistically-based, parameterizations. During the coming year, incorporation of the parameterizations into more physically realistic models that are being developed as part of MAP3S and verification of these models using data from the regional characterization studies will start to provide the models needed for undertaking more informed and acceptable assessments. Highlights of the results from Task 10 described in Chapter 12 include the following.

- A statistical-trajectory model has been developed that incorporates some of the physically realistic representations and is being used to provide estimates of the components of the regional sulfur budget.

- A trajectory model has been developed that calculates wet deposition of pollutants using observed hourly precipitation data and will permit comparison of model-predicted and observed deposition.

- Trajectory models have been used in assessment studies to show that the contribution of long distance transport of sulfate exceeds the local contribution and that emissions in the Ohio River Valley are important contributors to deterioriation of east coast air quality.

- A new numerical method has been developed that will allow formulation of a regional, grid-based model incorporating non-linear chemistry.

has undertaken several special activities. These are described in Chapter 13.

- A data bank has been established that makes data collected by MAP3S available to all interested researchers.

- A direct computer link has been established to the National Meteorological Center that allows direct access by MAP3S to meteorological data and will ultimately permit more up-to-date assessments and interpretation of experimental results.

- MAP3S cosponsored the International Symposium on Sulfur in the Atmosphere held in Dubrovnik, Yugoslavia in September 1977.

- A quarterly newsletter is now being sent to more than 500 interested people to allow for planning and interaction with other programs and rapid dissemination of available results.

1.5 FUTURE DIRECTIONS

Although substantial progress has been made, considerable work remains to be done. Of major importance in terms of assessing the current situation are the following:

- Continued operation of the eight-station precipitation chemistry network and the sulfate acidity network to better characterize properties of storms and air masses.

- More extensive analysis of air quality and precipitation chemistry data to identify particularly important episodes and events, source-receptor relationships and acidification mechanisms.

- Continued refinement of the emissions inventory, including incorporation of specific power plant data from the SURE program.

- Examination of spatial and temporal inhomogenieties that might influence the sub-grid parameterization of regional scale models.

Field experiments undertaken to date have raised questions as well as provided some answers. Coming experiments need to focus on the following processes and mechanisms:

Field experiments are needed as a step toward identifying the source of hydrogen ions in precipitation.

● Long distance horizontal transport through regions of complex terrain.

● Evolution of various types of polluted air masses under both stagnant and ducting conditions, including evaluation of the role of energy-related emissions on visibility.

● Identification of synoptic and micrometeorological conditions that would enhance long-distance transport.

The numerical modeling of regional pollution can be expected to make extensive progress as the effort to construct grid-type models continues and as data become available for model verification studies. Major efforts will include the following tasks:

● Develop a comprehensive, grid-type model incorporating real-time transport, transformation, and removal processes.

● Intercompare the results from the different types of models that have been and are becoming available to better understand the need for physically realistic representations.

● Compare model results to compilations of data that document day-to-day variation of regional air quality during periods of intensive measurement and high pollutant concentration.

● Develop the capability to model precipitation chemistry on a regional scale, including simulation of the acidity.

> Will the acidity of precipitation increase with increased combustion of coal?
>
> Can atmospheric concentrations of particulate sulfur be decreased by reducing sulfur oxide emissions?

2.1 RESEARCH OBJECTIVE

To improve the basis for answering such questions in energy and environmental planning, the Department of Energy's Office of Health and Environmental Research[*] (OHER) organized the Multi-state Atmospheric Power Production Pollution Study (MAP3S) in 1976. MAP3S was designed to provide the knowledge and scientific tools (e.g., numerical models) required to carry out improved assessments of the atmospheric effects of alternative strategies for generating power from fossil fuel. Such assessments are needed so that DOE can ensure that their energy policies adequately protect human health and preserve the environment.

The issues of top priority when MAP3S was initiated concerned combustion of coal. These issues are still of paramount importance. Coal is the most abundant domestic fossil energy. Its increasing use for electric power production, itself a major and growing sector of our energy economy, poses the potential for substantial increases in pollutant emissions, particularly in the high-population, energy-intensive, northeastern quadrant of the United States.[**]

Although there are several major categories of pollutants emitted from fossil-fuel power plants (see Table 2.1), both health and ecological effects studies and observations of air quality and precipitation chemistry indicated that sulfur oxides, particularly sulfate particulate matter, should be of primary interest. Thus, MAP3S has focused its attention on sulfur oxides in its initial phase. More recent effects studies and some research within MAP3S, however, are indicating that nitrogen oxides are of comparable significance both in their own right and because of the interacting role they play in determining the fate of sulfur emissions. Therefore, as MAP3S proceeds, increased emphasis is

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[*]Formerly Division of Biomedical and Environmental Research.

[**]This region, referred to as the Greater Northeast, includes the upper Midwest, the Northeast, and areas directly influencing air quality in

TABLE 2.1. Categories of Energy-Related Pollutant Emissions

- Sulfur oxides, sulfites, and sulfates.

- Nitrogen oxides and their secondary reaction products including oxidants.

- Hydrocarbons, including polycyclic organic matter.

- Trace inorganic elements.

- Particulate matter, which may contain any or all of the above substances and elemental carbon or soot.

2.2 RESEARCH APPROACH

MAP3S is using a multi-pronged approach to improve understanding of the atmospheric effects of energy related emissions.[*] The three major elements of MAP3S are:

- Regional Characterization,

- Field and Laboratory Experiments, and

- Numerical Modeling and Analysis.

Within these three program areas, ten tasks have been identified that must be addressed if scientific uncertainty is to be reduced (see Table 2.2). Although each task is identified with a particular program area, there is actually considerable overlap in objectives and therefore interaction among participants.

Regional characterization encompasses those tasks involved in determining the state of the current situation in the northeastern United States. This involves both inventorying pollutant emissions and measuring what pollutants are found in the air and precipitation - including development of techniques to make the needed measurements.

Regional Characterization

1. To specify and quantify the emissions of atmospheric energy-related (AER) pollutants from present power production plants, and to consider pollutants that may be emitted as a result of an increased usage of coal and the introduction of new power production processes, e.g., fluidized bed combustion and magneto-hydrodynamic (MHD) systems.

2. To identify and quantify sources of pollutants that do not stem directly from power production (e.g., transportation, residential, and industrial sources) but that may affect the concentration, distribution, transformation, and fate of AER pollutants.

3. To characterize the physical and chemical properties of AER pollutants commonly found in the atmosphere on a regional scale. These properties include particle size, oxidation state, derivative compounds, molecular form, etc.

4. To determine the spatial and temporal distribution of AER pollutants under both average and extreme conditions.

Field and Laboratory Experiments

5. To determine the processes and parameters governing the vertical and horizontal transport of AER pollutants.

6. To identify the chemical and physical transformation processes affecting AER pollutants, and to determine the rates and mechanisms controlling such processes.

7. To determine the rates of physical and biochemical mechanisms governing the removal of AER pollutants from the atmosphere at the earth's surface (dry deposition).

8. To identify the mechanisms and rates governing the removal of AER pollutants by precipitation scavenging, and to determine the effects of AER pollutants on trace material balances and precipitation chemistry, specifically the acid-base relationships.

9. To determine the effects of AER pollutants on weather and climate, including effects on visibility, radiation transport, and on the amount and extent of precipitation.

<u>Numerical Modeling and Analysis</u>

10. To develop, verify, and demonstrate methods (numerical models) that will make it possible to accurately simulate the atmospheric transport and transformation of AER pollutants for use in assessing various strategies for generating power.

Research within the program area of field and laboratory experiments focuses on improving understanding of specific processes that transport, transform, or remove pollutants from the atmosphere. In its broadest sense MAP3S objectives also include investigation of any effects that pollutants might have on weather and climate. A largely exploratory task is also included in this program element focusing mainly on influences of pollutants on visibility and precipitation mechanisms.

Numerical modeling and analysis provide the framework for relating what actually is happening with the mechanisms controlling pollutant budgets and cycles. MAP3S is attempting to develop improved numerical models that actually incorporate realistic representations of physical and chemical processes rather than relying on empirical "black box" relationships. This approach is based on the premise that only with detailed understanding of what is occurring can reliance be placed on model results that are to be used for planning optimum and effective emission control strategies.

Each program area relies on the others. Numerical modeling depends on field and laboratory experiments to provide and verify formulations for representing various physical and chemical processes and depends on characterization studies to provide the data needed for composite model verification. Results from highly focused field experiments must be tested in numerical model simulations to determine if they are consistent when applied to multi-process, regional-scale situations. The rationale for characterization studies is often based on inconsistencies evident in numerical models.

2.3 RESEARCH PRIORITIES

Before designing the specific MAP3S approach to conducting research in the three program areas identified in the preceding section, an assessment was made of both the thrust of other related programs and

network of surface stations (Perhac, 1978). Since that time EPA has initiated the STATE and VISTTA programs, efforts that focus on sulfur and visibility, respectively. For STATE, the research thrust involves major, comprehensive field experiments. The Atmospheric Environment Service of Canada has also initiated a comprehensive program, with major interest on trans-boundary transport (Whelpdale, 1978). At a number of meetings there has been extensive communication between these several programs including especially the jointly-sponsored International Symposium on Sulfur in the Atmosphere held in Dubrovnik, Yugoslavia in September 1977. With respect to the SURE program, detailed project interactions were planned as part of the development of the program (Mueller et al., 1978).

With respect to the second issue, that of resources available to DOE, initiation of MAP3S within DOE was part of an effort to broaden the prior emphasis of the AEC (predecessor to ERDA, in turn the predecessor to DOE) on the transport and fate of radionuclides. As such MAP3S involved primarily the redirection of already supported research capabilities within the national laboratories and long-term contractor research groups, including the universities. The major thrust of these activities involved tightly focused field experiments coupled with numerical simulation.

Together, these factors have led MAP3S to allocate its efforts among the three areas in the following manner:

- Regional Characterization: Cooperate with and augment efforts of EPRI to determine regional air quality. Establish networks to monitor precipitation chemistry and aerosol acidity. Develop a regional emissions inventory.

- Field and Laboratory Experiments: Emphasize focused field experiments that examine the influences of particular processes. Conduct limited regional experients to examine interaction of processes. Rely largely on EPA to support laboratory research on transformation mechanisms.

- Numerical Modeling and Analysis: Emphasize efforts to develop models that realistically treat physical and chemical processes, going beyond more highly parameterized approaches of other groups. Analyze available data and results of focused field experiments as part of model verification studies.

These activities are not meant to be mutually exclusive; rather within

the resources of the DOE program and the several related programs taken together, so that, a broad-based, comprehensive national research effort is being pursued.

The efforts being undertaken in pursuit of these objectives form the basis for this report. This report is not meant to be a complete exposition of the state of science in this area, rather a description of research contributions made by the MAP3S program, and, in some cases, related research carried on by MAP3S investigators. Comments in each chapter, however, attempt to interrelate the MAP3S efforts with those of the other programs and to provide a perspective on the importance of the research. A concluding chapter (Chapter 14) evaluates how much further we still need to go, in terms of both the uncertainty in current understanding and the even more complex questions that this, and related, research programs seem to be raising.

2.4 ALLOCATION OF RESOURCES

Although the major thrust of this report is to describe scientific progress, a brief review of the financial resources being committed by DOE may provide a useful framework for evaluation. The total MAP3S budget for FY-1978 was approximately $3.8 M, up from about $3.2 M in FY-1976. These funds have been allocated among the ten task areas described earlier as shown in Table 2.4. These figures are somewhat approximate since we have, within the participating groups, made efforts to closely couple observations, experiments and modeling. We should also note that the amount of funding alone is not necessarily a good measure of the importance of the activities within that area since some types (e.g., field experiments) are much more expensive than others. Further, some of the MAP3S efforts are jointly sponsored by other agencies or programs, and Table 2.4 reflects only funding from the Office of Health and Environmental Research of DOE.

In broad terms, during FY-1978, one-third of the budget is allocated to regional characterization, one-half to focused field experiments, and one-sixth to numerical modeling and analysis. With the completion of the major part of the SURE measurement program in October 1978, and with the accomplishment of several field experiments, the next two years should see increased emphasis on analysis, interpretation and modeling. Building on the theoretical consolidation that can be expected from these efforts, however, there will be a continuing need for characterization and field experiment programs that can address the many new questions that are arising. Chapter 14 attempts to aim the MAP3S program in these challenging directions.

Regional Characterization:

- Develop an up-to-date source emissions inventory.

- Improve aerosol instrumentation to better define pollutant characteristics.

- Augment SURE surface measurement program with network of instruments to determine sulfate acidity.

- Cooperate with SURE aircraft program to better define vertical distribution of pollutants. Also undertake separate special studies as needed.

- Establish network to measure precipitation chemistry.

- Undertake quality assurance and instrument evaluation programs to improve understanding of limits of present capabilities.

Field and Laboratory Experiments

- Measure diurnal behavior of planetary boundary layer and develop better prescription for representing its effects on vertical mixing.

- Develop improved capabilities for inert tracer measurements to be used in experiments that better define role of horizontal transport.

- Develop and evaluate better means for representing horizontal transport of pollutants.

- Measure pollutant transformation in power plant plumes, smelter plumes, urban plumes and free atmosphere as basis for improving numerical representation.

- Measure pollutant removal rates as function of surface type and atmospheric characteristics so as to provide basis for improved numerical representation.

- Measure pollutant removal in various precipitation regimes and develop representation for use in numerical models.

Numerical Modeling and Analysis

- Improve existing models and develop new models by incorporation of more differentiated descriptions of transport, transformation and removal processes of AER pollutants embodying the results of research conducted within MAP3S and

- Develop improved techniques for executing these models.
- Verify the simulative capability of these model by carrying out comparison of model results with characterization measurements.
- Evaluate the uncertainties in the modeling capability that is achieved and indicate needed areas of future research.

TABLE 2.4. Allocation of MAP3S Resources

Task	Percent of Resources[*]
1. Power production emissions	} 2%
2. Non-power production emissions	
3. Pollutant properties	10%
4. Pollutant distribution[+]	20%
5. Pollutant transport	10%
6. Pollutant transformation	20%
7. Surface removal processes	2%
8. Wet removal processes[+]	20%
9. Weather and climate modification	1%
10. Numerical modeling and analysis	15%

[*]Figures are to nearest 5%, except for categories receiving less than 5%.

[+]The costs for precipitation chemistry network operations are now included under Task 4 rather than Task 8 as done in MAP3S Program Plan.

MacCracken, M. C., "MAP3S: An Investigation of Atmospher
Energy-Related Pollutants in the Northeastern United States," At
Environ., 12, 649-659, 1978.

Mueller, P. K., G. M. Hidy and E. Y. Tong, "Implementation a
Coordination of the Sulfate Regional Experiment (SURE) and Relat
Programs," EPRI Report, Palo Alto (in press), 1978.

Perhac, R. M., "Sulfate Regional Experiment in Northeastern Unit
States: the 'SURE' Program," Atm. Environ. 12, 641-647, 1978.

Whelpdale, D. M., "Large-Scale Atmospheric Sulfur Studies in Canada
Atm. Environ., 12, 661-670, 1978.

Wilson, W. E., Jr., "Sulfates in the Atmosphere: A Progress Report
Project MISTT," Atm. Environ., 12, 537-547, 1978.

The annual emissions of sulfur from stationary sources, both power production and industrial, total about 5×10^{11} moles with more than three-fourths being emitted in the northeastern part of the United States. An improved emissions inventory for power plants is being obtained as a result of the combined efforts of the MAP3S and SURE programs.

Essentially all of the sulfur is emitted as sulfur dioxide. The amount emitted as sulfate is believed to be small, but is not well known, in part because of deficiencies that have existed in the measurement technique and in part because of the variabilities in plant operating conditions. However, it is now recognized that a well maintained coal (Forrest and Newman, 1977) or oil fired power plant (Forrest et al., 1979) can keep the sulfate emissions under 2% and, at times, even below 1% of the sulfur dioxide emissions. Using new measuring probes, measurements of the percentage of sulfate emitted at the breech of power plants are indicating a range of between 1-2%. A range of 2-3% is found via aircraft measurements within 1-2 km of the source. These observations can be considered to be in substantial agreement.

The procedure developed for breech measurements is described below and that for plume measurements in Chapter 8.2. An investigation has also been conducted on attempting to correlate primary sulfate production with fuel composition and power plant operating characteristics.

3.1 DIRECT MEASUREMENT OF STACK EMISSIONS*

Any voluntary or legislated action taken to control sulfates should be based at least in part on a thorough knowledge of the character of primary sulfates, their emission rates from power plant, institutional, and industrial boilers as well as from apartment and home heating units, and an understanding of the principal variables that govern the magnitude of those emissions. Both for consideration of potential health effects and for determination of the mechanisms and parameters that affect the magnitude and distribution of such emissions, the character of

determined with flue gas sampling methods that differentiate between the acid form and the less nocuous sulfates. Two programs have been conducted at BNL with goals of validation of sampling procedures and correlation of the emissions of H_2SO_4 and metal sulfates (MSO_4) in terms of the most significant operating parameters. Both goals have, in most part, been achieved.

3.1.1 Sampling Methodology

A reliable sampling method utilizing a Brookhaven-designed nozzle and filter assembly for collection, in situ, of flue gas particles (including water soluble metal sulfates) followed by a version of the Goksoyr-Ross condenser coil for separate collection of the flue gas sulfuric acid has been laboratory validated and field tested at four oil fired and one coal fired power plant units (Dietz and Wieser, 1977, 1978a, 1978b; Goksoyr and Ross, 1962; Dietz and Garber, 1977). Basically the controlled condensation system (CCS) (see Fig. 3.1) consisted of an in situ filter (for collection of particulate matter) located directly behind the isokinetically sized nozzle, a partially heated glass probe terminating in a 17-turn 6 mm glass coil maintained at 140°F for collection of the H_2SO_4 aerosol, a back-up pyrex wool plug, a 10-turn coil and receiver vessel maintained at ice water temperature for condensing most of the water vapor, two impingers containing peroxide for collection of SO_2, and finally a drier, pump, and dry test meter. An evacuated bottle was used to collect a 20-minute sample of the processed flue gas for subsequent determination of CO and O_2 levels, the latter being used to correct for flue ducting and heat exchanger air leaks. A quartz fiber back-up filter has subsequently been added because of documented evidence of H_2SO_4 breakthrough of the glass wool plug (Dietz and Wieser, 1978b). Complete details of design and validation will be available elsewhere, including documentation of the $> 95\%$ recovery of sampled H_2SO_4 (Dietz and Wieser, 1979).

As presently recommended, the other prominent sampling method, the modified version of the EPA Method 6, does not provide for specific determination of particulate metal sulfates and H_2SO_4 (Cheney et al., 1977; U. S. EPA, 1976). A Brookhaven modification (BM6), utilizing the same isokinetically-sized nozzle and filter assembly as for the Brookhaven CCS, allowed the sulfuric acid only to pass through the filter for subsequent collection in the modified isopropyl alcohol (IPA) midget bubblers and filter assembly as shown in Fig. 3.2. The IPA was supposed to preferentially dissolve H_2SO_4 while at the same time inhibit the oxidation of dissolved SO_2. Unfortunately, three problems were encountered with the use of this approach. The trace amount of SO_2 that did dissolve in the IPA was not readily stripped from the solution by the recommended 12 to 15 liters of ambient air as shown by the results in

FIGURE 3.1 Schematic diagram of BNL controlled condensation scheme.
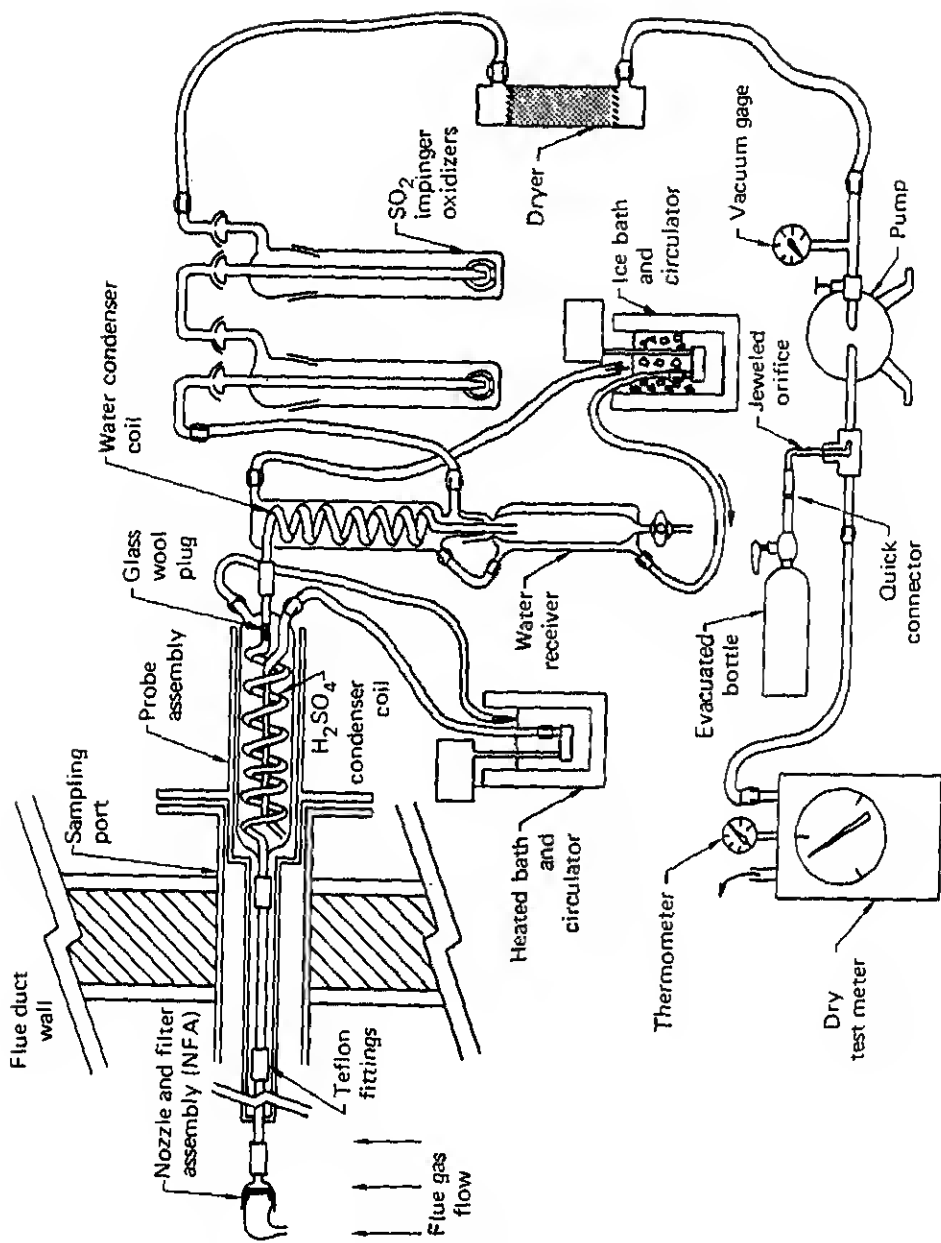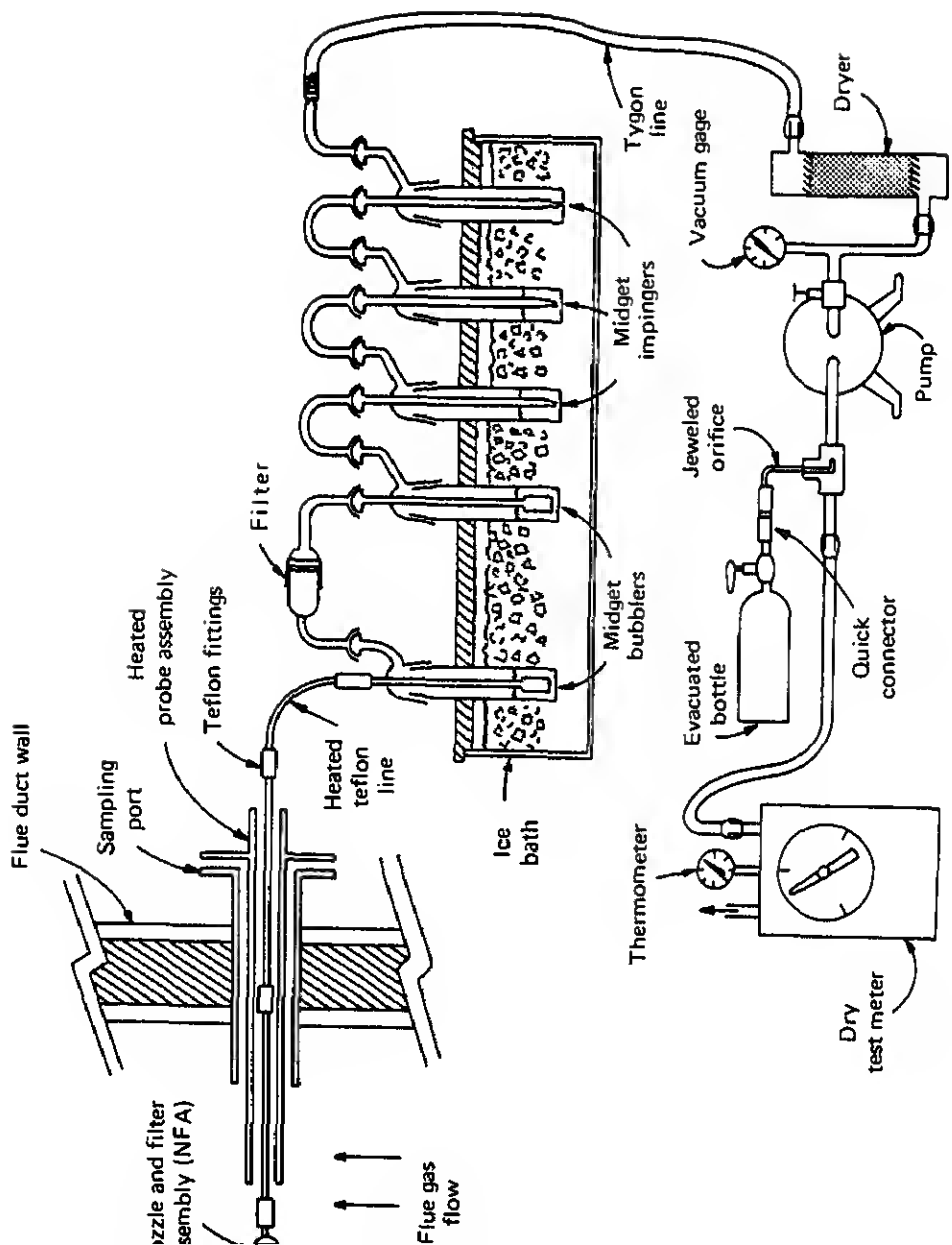
FIGURE 3.2 Schematic diagram of BNL method 6 apparatus.
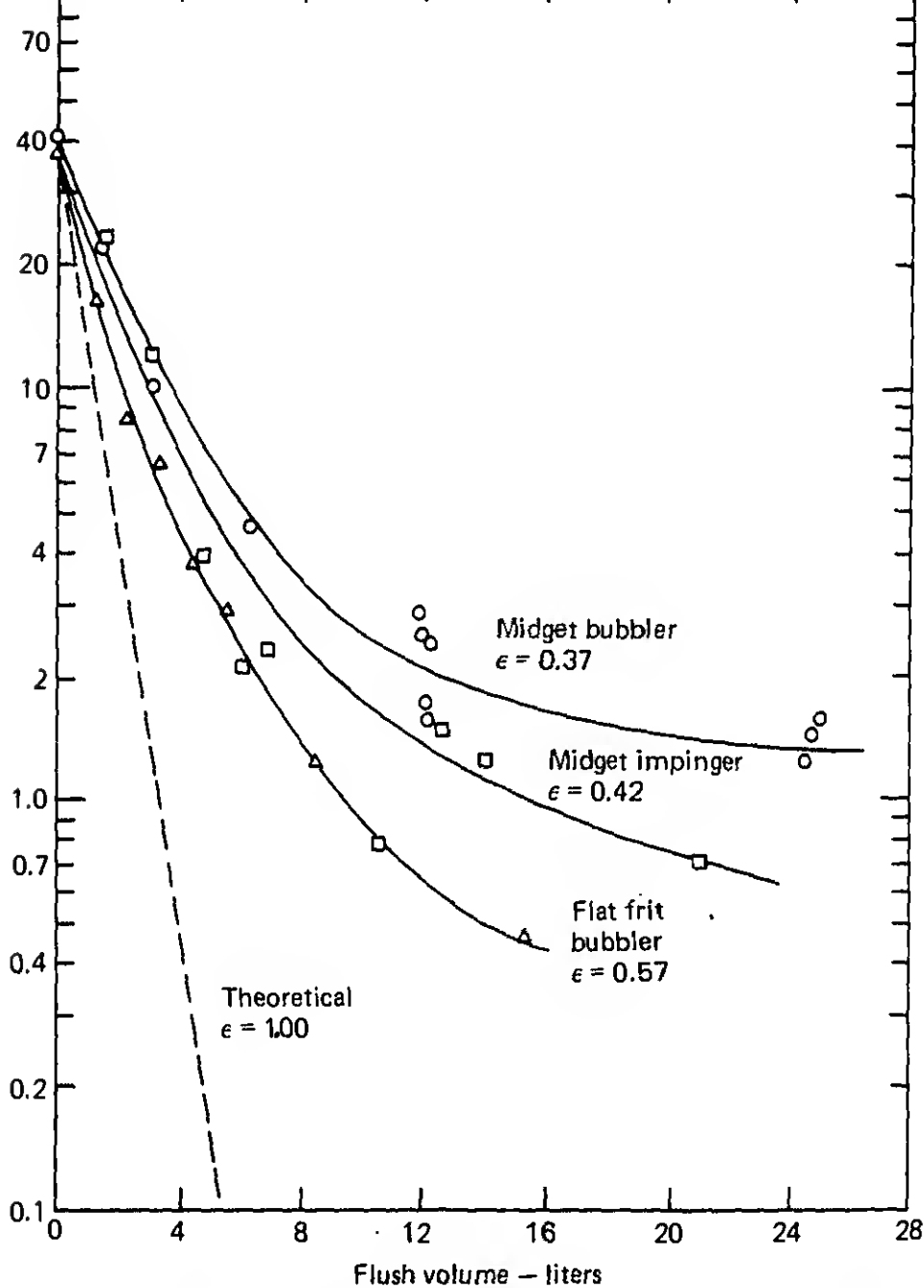
FIGURE 3.3 Residual dissolved SO₂ as apparent flue gas H₂SO₄ versus

Thus, the use of the IPA midget bubbler approach can lead to gross positive errors in H_2SO_4 determinations, especially at sources where low emissions (<3 ppm) are encountered. A complete study of this method was recently concluded and presented elsewhere (Dietz et al., 1978a).

As a result of these problems, it was concluded that further use of the IPA approach, even the BM6, for determination of sulfuric acid at power plants should be discontinued. The working group on measurement of gaseous sulfur oxides emissions recently concluded that "it is not possible to measure H_2SO_4 concentrations less than 1 vol. ppm in flue gas using IPA methodology (e.g., EPA Modified Method 6 or Method 8)" (Dietz, 1978). Similarly it was concluded that "the controlled condensation methodology is the preferred approach for manual determination of H_2SO_4." Thus the Brookhaven CCS has been the mainstay for measuring emissions with the goal of correlating the effects of the most significant operating parameters.

3.1.2 Field Sampling Experience

From March 1977 through July 1978, a total of 107 flue gas sampling measurements were obtained at the Long Island Lighting Company Northport and Barrett Power Stations. Conditions at the oil fired units varied from 0.0 to 4.0% furnace O_2, fuel sulfur from 0.3 to 2.6%, fuel vandium (a catalyst for production of H_2SO_4) from 10 to 460 ppm, power levels from 1/2 to full load, Liquimag corrosion inhibitor (MgO) from 10 to 840 ppm Mg (by wt. of the fuel), and electrostatic precipitator (ESP) efficiency from 0 to 95%. As a result of these variations of the operating parameters, H_2SO_4 emissions were found to vary from 0.01 to 40 ppm and MSO_4 emissions from 1 to 27 ppm (4 to 110 mg/m^3). Total sulfate emissions varied from 0.10 to 5.0% of the sulfur in the fuel.

The minimum sulfate emission occurred at full load (356 MW) with 2.4% S in the fuel oil. The maximum sulfate emission occurred at nearly full load (325 MW) with 2.1% S in the fuel oil. What, then, accounted for the nearly 40-fold difference in total sulfate emissions? In the former case, furnace oxygen was 0.0% limiting H_2SO_4 to only 0.4 ppm and the ESP was operating at 91% efficiency, limiting MSO_4 to 1.1 ppm. In the high emissions case, furnace oxygen was 2.7% yielding H_2SO_4 of about 37 ppm and, since the unit had no ESP, the level of emitted MSO_4 was about 23 ppm. It is quite obvious that a single factor representing the emissions of total sulfates in developing regional emissions inventories could be in substantial error and would also make no distinction between the acid form and the metal sulfates.

For a week in August 1978, 17 flue gas measurements were made at the Tennessee Valley Authority Cumberland Power Plant (Unit 2) as part

concentrations ranging from 2200 to 2600 ppm - about 65% higher than the typical Northport oil fired units. At the electrostatic precipitator (ESP) inlet, the H_2SO_4 was 25 to 27 ppm at the 5% furnace oxygen level (constant for the entire week). At the ESP outlet, H_2SO_4 ranged from 9 to 18 ppm (average of 13.5 ppm H_2SO_4), indicating that the ESP was indirectly responsible for about a 50% reduction in acid emissions. The acid level was only about 1/3 of what would have been anticipated for an oil fired unit under the same conditions. Since the vanadium content in coal was an order of magnitude less than that in the Northport oil, another element must have been responsible for the apparent catalytic activity.

Particulate matter at the ESP inlet of the coal fired unit was about 22000 mg/m^3 and at the outlet ranged from 150 to 500 mg/m^3 (average of 309 mg/m^3) for an average ESP efficiency of 98.6%. Metal sulfates ranged from 20 to 34 ppm (80 to 140 mg/m^3 or about 0.5% of the total particulate matter) at the ESP inlet and from 1.0 to 4.6 ppm (4.1 to 18.6 mg/m^3) for an average of 2.6 ppm (10.4 mg/m^3) or 3.4% of the total particulate matter at the ESP outlet. The 7-fold higher percentage sulfate content associated with the particulate matter at the ESP outlet would tend to imply that particulate sulfates were associated with particles of a size not as efficiently removed by the ESP as the major particulates.

The total emissions of sulfuric acid and metal sulfates from that coal fired unit, expressed as a percentage of the total sulfur in the fuel, ranged from 0.43 to 0.81% with an average emission of 0.64 ± 0.13% of the fuel sulfur. Of those sulfate emissions, on the average, 84% was in the form of sulfuric acid. The total sulfate emissions were much less than expected and it was surprising to see so much in the form of H_2SO_4. Most of the sulfate emissions were expected to have been in the form of metal sulfates because of the high ash content.

3.1.3 Parameters Affecting Sulfate Emissions

For a particular power plant unit burning a specified fuel oil, the two most important parameters governing the emissions of H_2SO_4 and MSO_4 were the furnace oxygen level and the efficiency of the ESP. The reduction in MSO_4 emissions with increasing ESP efficiency is shown in Fig. 3.4. At greater than 90% efficiency, it is possible to keep MSO_4 emissions below about 0.1% of the sulfur in the fuel.

Furnace oxygen was demonstrated to have a direct and almost linear effect on flue gas sulfuric acid concentration as shown by the results for Unit 3 at Northport (cf. Fig. 3.5). Similarly, as shown in Fig. 3.6, the
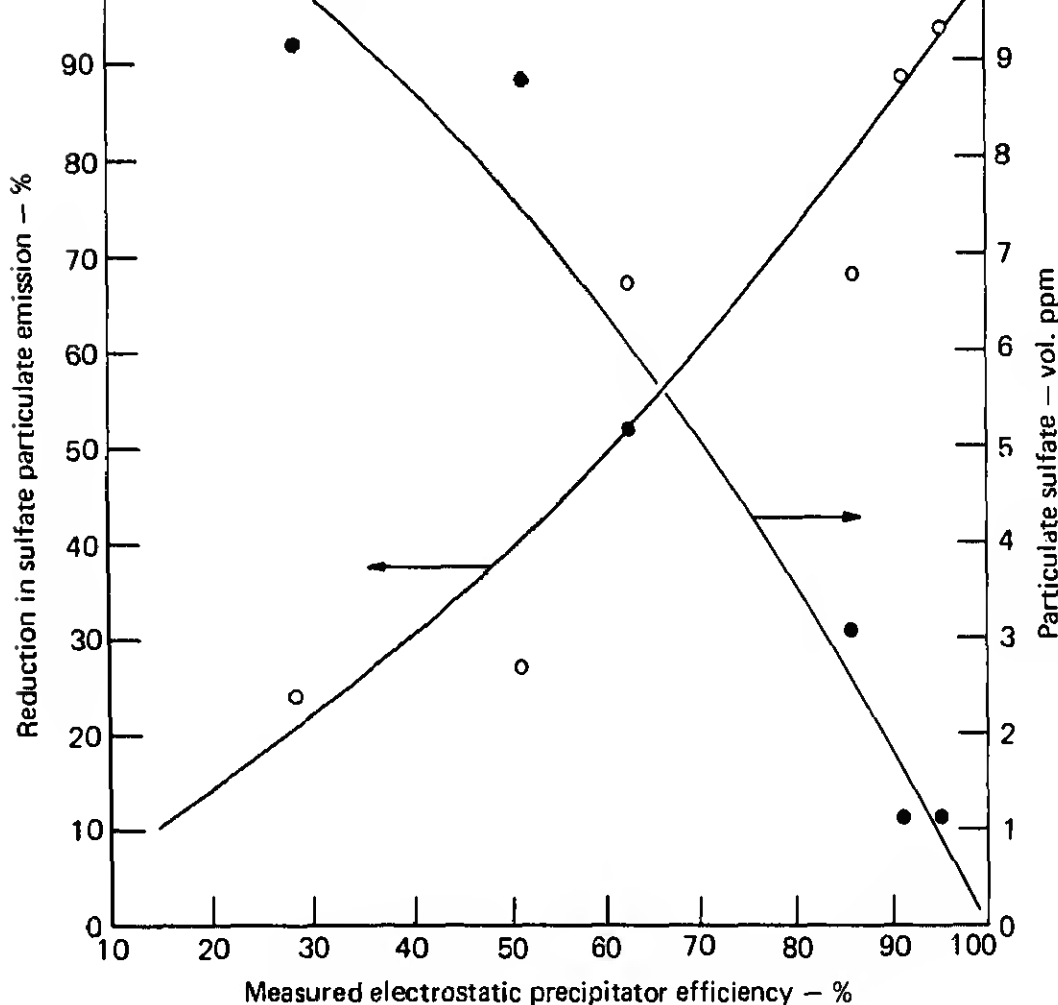
FIGURE 3.4   Effect of electrostatic precipitator efficiency on emission of primary metal sulfates.

slope between the lines for the two units has been attributed primarily to the difference in vanadium content in the fuel - higher for Unit 2. The effect of fuel vanadium and other ash constituents is discussed in the next section. The curvature demonstrated by the data for Unit 2 is also predictable - due to the dilution effect of increasing combustion air on both the reactant, SO_2, and the product, H_2SO_4.
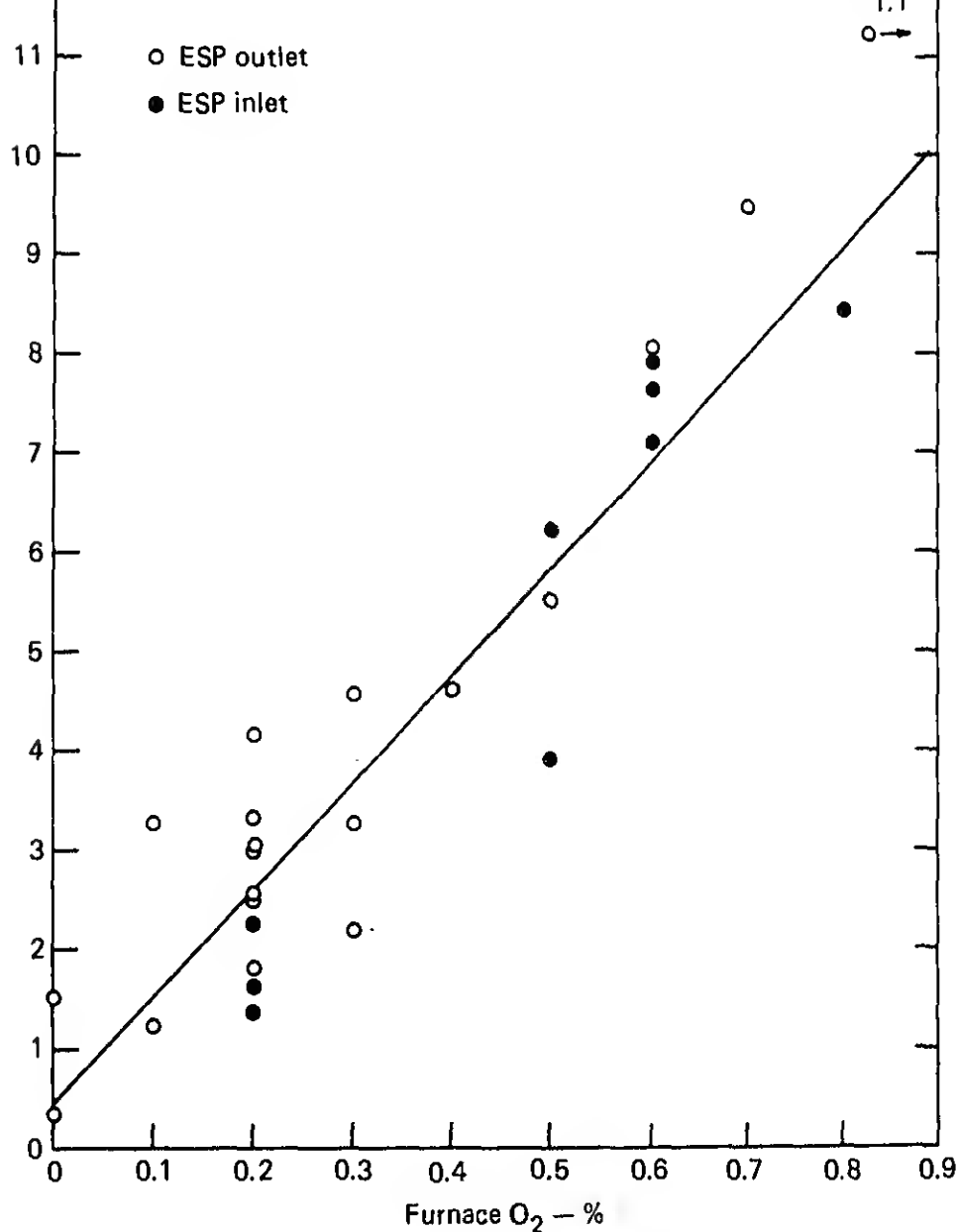
FIGURE 3.5 Effect of furnace oxygen on flue gas sulfuric acid emissions: medium H_2SO_4 range.
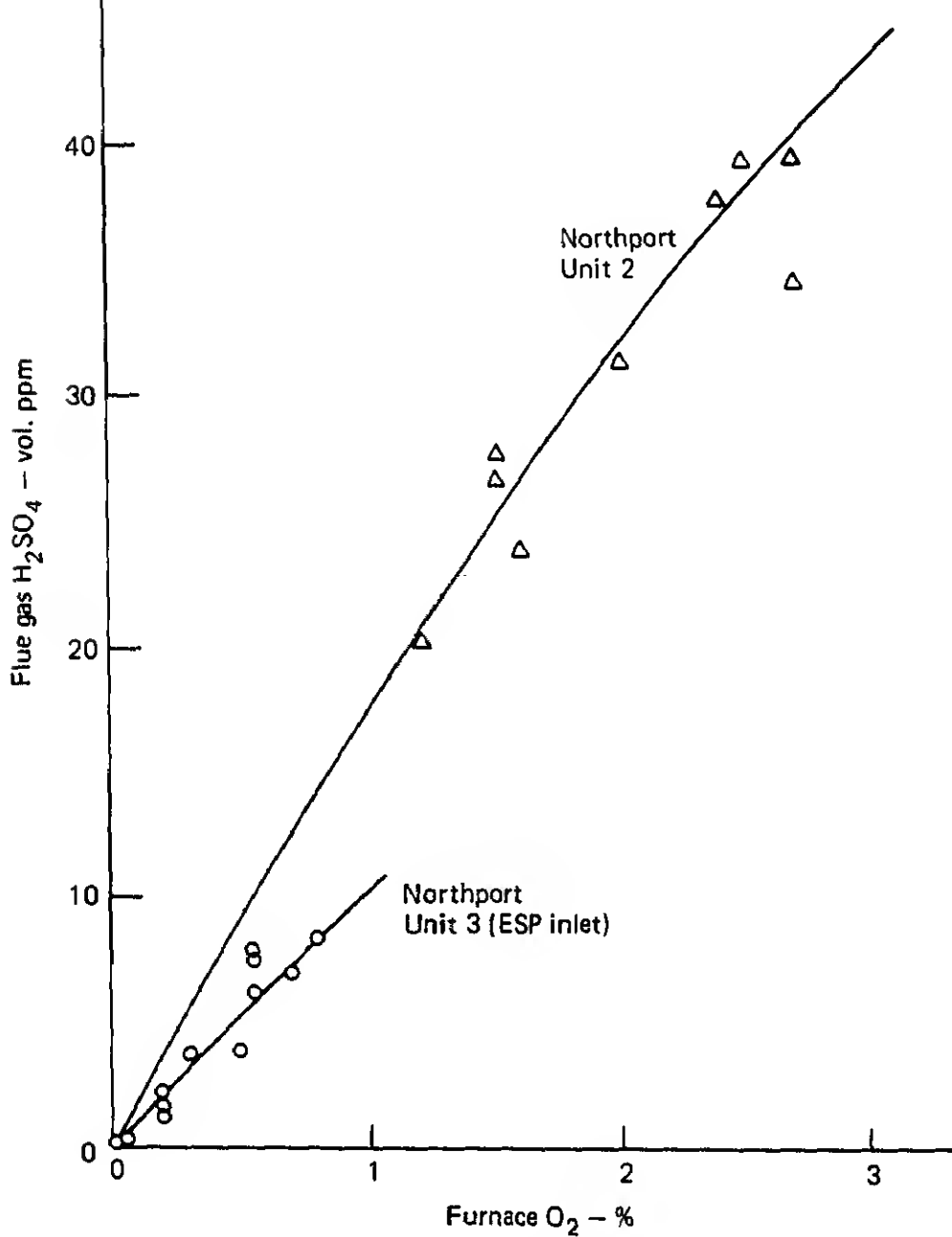
FIGURE 3.6 Effect of furnace oxygen on flue gas sulfuric emissions: high H_2SO_4 range.

A1, A2 and W. Similarly, the Brookhaven results at Barrett were in excellent agreement with the EPA results at a very similar plant M.

The results depicted in Fig. 3.7 confirmed the existence of an intercept for particulate metal sulfate formation at zero furnace oxygen, i.e., in the absence of sulfuric acid. The figure also demonstrated the dependence of metal sulfates on furnace oxygen levels as well as the sulfur and vanadium content of the fuel. The magnitude of the metal sulfate level at Barrett and plant M was lower than that at the other plants because the fuel sulfur content was less. The dependence of the metal sulfate concentration on furnace oxygen level, that is, the slope of the line, was much less than the other because of the much lower vanadium content.

Of the 107 flue gas measurement tests performed from March 1977 to July 1978, a total of 31 were completely analyzed for metal and carbon content of the particulate matter. In almost every case, an excellent material balance was achieved when compared with soluble sulfate measurements and gravimetric determinations, indicating self-consistency of the data. The results of the element determinations have provided very useful information and insight into the regions of sulfate formation, the distribution of elements between smaller and larger particles, the efficiency of the ESP for retaining the elements within the furnace system, the role of MgO as an H_2SO_4 and metal sulfate controls parameter, and the formation of a correlation for predicting the emissions of acid and sulfates.

3.1.4 Predicting Sulfate Emissions

All of the aforementioned 107 measurement runs are being carefully analyzed to establish a reliable basis for predicting the emissions of H_2SO_4 and metal sulfates as a function of parameters including power level, furnace oxygen, fuel oil sulfur, vanadium, sodium, and total ash content, MgO additive, electrostatic precipitator efficiency, and furnace gas soot or carbon content. Although the data analysis has not been completed for the correlation of metal sulfate emissions, that for H_2SO_4 has been formulated as shown by the following equation

$$[H_2SO_4] = \frac{1300 \; L \; [O_2] \; [S]}{(7.07 + 0.32 \; [O_2])^2} \cdot \frac{[V]}{([V] + [Mg] + [Na] + \frac{1}{2} [C])}$$
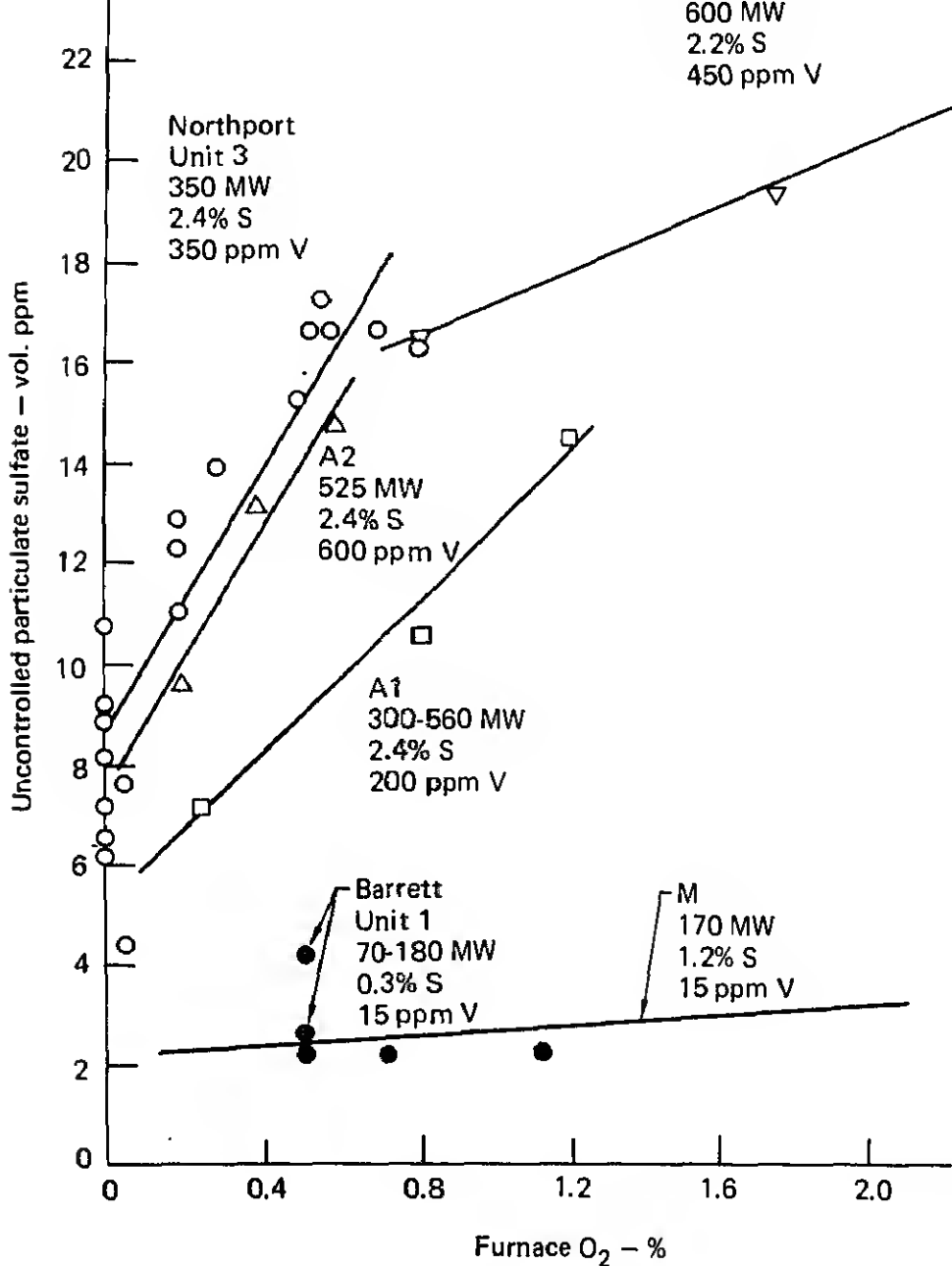
FIGURE 3.7 Effect of furnace oxygen and fuel oil sulfur and vana. content on the formation of metal sulfates at sever. fired units.

level); $[O_2]$ is the furnace oxygen (vol. %); $[S]$ is the sulfur content in the fuel (wt. %); $[V]$, $[Mg]$, and $[Na]$ are the vanadium, magnesium, and sodium content, respectively, in the fuel (wt. ppm); and $[C]$ is the unburned carbon content of the fuel (wt. ppm) as determined from typical flue gas particulate analyses. The latter carbon parameter may be a function of the furnace oxygen level and burner conditions but may also be related to the asphaltene content of the oil (O'Neal, 1978).

For all the runs at which furnace oxygen equaled or exceeded 0.5% and fuel vanadium content exceeded 75 ppm (i.e., 41 of the 107 runs), the equation predicted the H_2SO_4 levels, on the average, to within ± 25% of the measured values. For the balance of the runs where O_2 was between 0.2 and 0.4%, the prediction capability was to within ± 50%; at lower O_2 levels, the error in the measurement of the furnace oxygen (± 0.1 to 0.2%) prevailed.

The correlation successfully covered the range of parameters shown in Table 3.1. It correctly and quantitatively predicted observed changes in H_2SO_4 values during unusual circumstances. For example, in one series of measurements on two consecutive days, the soot level in the flue gas was unusually high, equivalent to 5000 to 6000 ppm of unburned carbon. If the carbon content had been its "normal" value, the predicted acid level would have been 13 ppm instead of the predicted value of 4.5 (measured was 4.7 to 6.3 ppm). At another time, the magnesium oxide additive pump became plugged and very little MgO was added to the fuel (only 11 ppm). If the "normal" MgO had been present, the equation predicted the H_2SO_4 would have been 16 ppm instead of the predicted 27 ppm at the reduced MgO level (measured acid was 23.3 ± 1.5 ppm). And finally, in the most unusual case, power level was 50% of full load; vanadium, 25% of normal; sulfur, 30% of normal. If all conditions had been normal, the predicted acid level would have been 38 ppm instead of the actual predicted level of 1.8 ppm (measured acid was 1.9 ± 0.2 ppm).

3.1.5 Conclusions and Discussion
The field utilization of the Brookhaven controlled condensation system at several oil-fired power plant units demonstrated the capability of a reasonably simple but quite reliable approach to the sampling of flue gas for the specific constituents, H_2SO_4 and total particulate matter; the latter was subsequently separated into a water soluble and insoluble fraction. The soluble fraction was shown to be entirely composed of water soluble metal sulfates - principally of Mg, V, and Na. Carbon was the main element in the insoluble fraction, which also contained metal oxides primarily of Mg, V, and iron.

| Parameter | Parameter Range | | |
	Minimum	Unit 3 Norm[*]	Ma
[H_2SO_4], vol. ppm	0.1	4.5	
L, fraction of full power	0.39	0.96	
[O_2], vol. %	0.1	0.25	
[S], wt. %	0.31	2.5	
[V], wt. ppm	4.0	400	
[Mg], wt. ppm	11	600	
[Na], wt. ppm	32	100	
[C], wt. ppm unburned	230	500	6

[*]LILCO Northport Unit 3 "normal" conditions.

emission of total sulfates was specific for H_2SO_4 and metal sulfat
exact nature of the mechanisms responsible for the variability of
emissions would have been more difficult to ascertain.

As a result of these two years of experimental field measurem
correlation for predicting H_2SO_4 emissions has been successfully c
providing a demonstrated reliability of better than ± 25%. It sh
emphasized that although the correlation is empirical in nature, i
entirely without a foundation based on expected effects of pa
parameters. Further evaluation of the field data will shortly pr
correlation for the emissions of metal sulfates.

A significant result of this study is the clear indication that
impact of primary sulfate emissions (i.e., sulfuric acid and
sulfates) in regions of the country are to be appropriately a
especially with an aim toward predicting the impact of further gr
fossil fueled combustion sources, a simple approach of assumin
sulfate emissions to be a portion of the sulfur in the fuel (e.g., 2%
fuel S) could be non-representative of the important parameter
health-effects and property damage standpoint.

If yes, and we suspect that is the correct answer, then several other questions arise:

1. Should total sulfate emissions be controlled, or just sulfuric acid, or should separate limits be placed on both the acid and the metal sulfates?

2. Should the vanadium content of fuel oil be limited? Sulfuric acid emissions are directly related to the vanadium.

3. Should furnace oxygen be limited in order to control sulfuric acid emissions?

4. Is the control of plume opacity a sufficient measure for controlling sulfuric acid emissions? Opacity can be due to particulate emissions as well as sulfuric acid aerosol.

Regardless of steps ultimately taken to control primary sulfuric acid emissions, the derived correlation at the very least provides plant operators with the necessary direction in which to change operating parameters in order to effect a decrease in H_2SO_4 formation and emission for compliance with regulations. In addition, the effect of increased utilization of oil fired power plants on the emission of sulfuric acid in certain regions of the country can now be more quantitatively assessed. Similar correlations for coal fired units as well as for power plants equipped with flue gas desulfurization (FGD) systems should be derived.

3.2 DEVELOPING A POWER PRODUCTION EMISSION INVENTORY

Initial data on power production emissions in the Greater Northeast have been obtained from BNL's Regional Energy Study Program (RESP), which in turn compiled the data from the EPA's National Emissions Data System (NEDS). Based on experience gained during the RESP activities, however, a number of actions were taken to permit continued effort to improve the data base.

- An inter-agency agreement between EPA and DOE (then ERDA) to allow BNL direct access to EPA's National Computer Center was continued in force. (The agreement also permitted access to all data and programs of the National Aerometric Data Bank (NADB), data that would assist in later model verification studies.)

power production emission data. State and local agencies have also been contacted for additional information.

- Because of the diversity of the expected uses of the emissions data, a generalized Data Base Management System has been implemented at BNL to manipulate the computerized inventories. Prototype data bases were designed and loaded using the NEDS point source emissions data for all states east of the Mississippi River. Both power production and nonpower production point sources (see also Sec. 4.1) were combined into one inventory, but identification by source type was maintained.

Early in MAP3S, FPC Form 67 data were obtained for the years 1969 to 1974. Later data will be requested as soon as they are available. Although these data are prior to the MAP3S study period, they do allow qualitative comparison with the NEDS data and will serve until data become available from the special SURE power plant emissions survey being conducted by GCA.

To facilitate user access to power production emissions data, a summary of pertinent FPC data was incorporated into the NEDS based inventory data bases. The choice of what to include in this data summary was a compromise between data most frequently accessed and size considerations for the data bases. This choice is subject to revision if necessary. Air quality data from the FPC Form 67, which can supplement NADB data, have also been data banked and are available as separate data bases.

Future work specific to the power production section of the inventory includes checks to insure correspondence between sources listed by NEDS and sources listed by FPC; comparison of emissions and fuel data between these two sources, and a search for additional sources of data to insure completeness and accuracy of the inventory. Table 3.2 lists the number of power plants as included in the NEDS and FPC emission inventories – obviously effort must be devoted to developing a consistent data base.

Figure 3.8 shows the locations of the 500 largest SO_2 emitting power plants in the eastern United States, as included in the MAP3S emissions inventory. For further details on the development of the emissions inventory, see Chapter 4.1.

	NEDS DATA	FPC DATA
	# plants with electric power SIC* codes	1974 # plants
Alabama	2	15
Connecticut	27	11
Delaware	4	4
Florida	35	44
Georgia	14	15
Illinois	48	43
Indiana	47	29
Kentucky	17	21
Maine	10	4
Maryland	16	12
Massachusetts	28	18
Michigan	58	31
Mississippi	12	13
New Hampshire	7	3
New Jersey	26	20
New York	58	34
North Carolina	14	17
Ohio	29	39
Pennsylvania	60	42
Rhode Island	4	2
South Carolina	14	14
Tennessee	8	8
Vermont	4	2
Virginia	14	14
Washington, D. C.	2	2
West Virginia	12	13
Wisconsin	27	25

*SIC - Standard Industrial Classification.

POWER PLANT LOCATIONS

MAJOR DATA MANAGEMENT
BROOKHAVEN NATIONAL LAB
UPTON NY 11973

LONGITUDE

LATITUDE
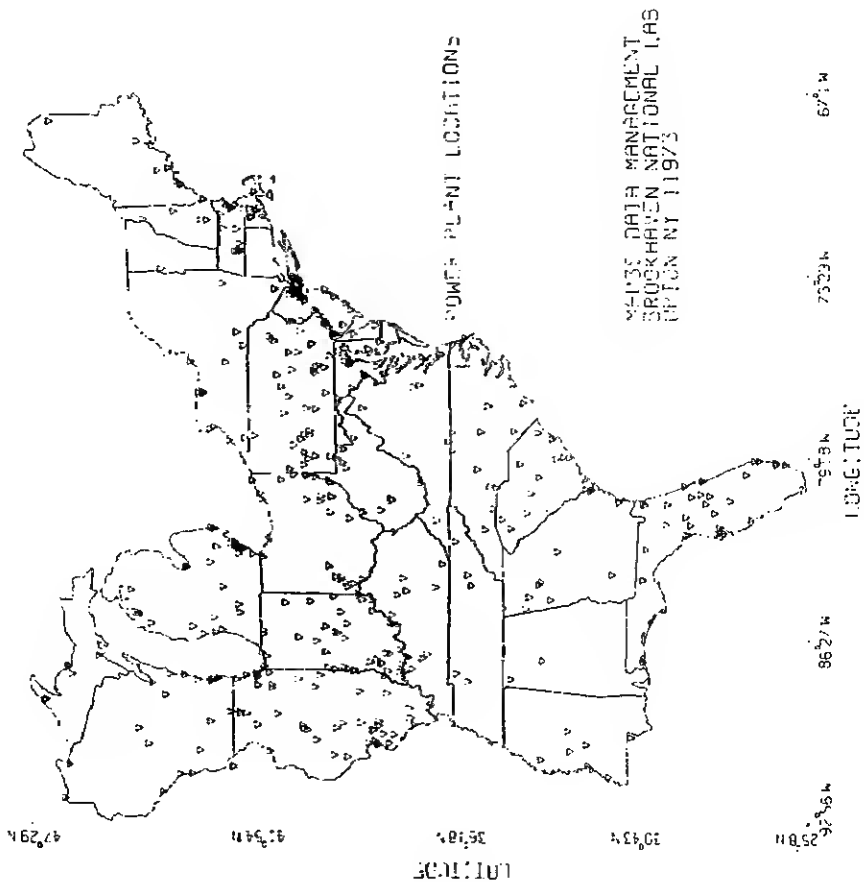
Cheney, J. L., W. T. Winberry and J. B. Homolya, "Evaluation of a Method for Primary Sulfate Emissions from Combustion Sources," _J. Environ. Sci. Health_, _A12_(10), 549-66, 1977.

Dietz, R. N., "Report of the Working Group on Measurement of Gaseous Sulfur Oxide Emissions," in _Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources, EPA-600/9-78-020a_, pp 137-141, August 1978.

Dietz, R. N. and R. W. Garber, "Power Plant Flue Gas and Plume Sampling Studies," Brookhaven National Laboratory Progress Report No. 1, November 1977.

Dietz, R. N. and R. W. Garber, "Power Plant Flue Gas and Plume Sampling Studies," Brookhaven National Laboratory Progress Report No. 2, Informal BNL Report BNL-25420, December 1978.

Dietz, R. N. and R. F. Wieser, "Sulfate Emissions from Fossil Fueled Combustion Sources," Brookhaven National Laboratory Progress Report No. 5, September 1977.

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Dietz, R. N. and R. F. Wieser, "Sulfate Emissions from Fossil Fueled Combustion Sources," Brookhaven National Laboratory Progress Report No. 7, October 1978b.

Dietz, R. N. and R. F. Wieser, "Sampling Power Plant Flue Gas: Separate Collection of Suspended Particulates and Sulfuric Acid," Brookhaven National Laboratory Report (in preparation), 1979.

Dietz, R. N., R. F. Wieser, and L. Newman, "An Evaluation of a Modified Method 6 Flue Gas Sampling Procedure," in _Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources, EPA-600/9-78-020a_, pp 3-25, August 1978a.

Dietz, R. N., R. F. Wieser, and L. Newman, "Operating Parameters Affecting Sulfate Emissions from an Oil-Fired Power Unit," in

Forrest, J., R. Garber and L. Newman, "Formation of Sulfat Ammonium and Nitrate in an Oil-Fired Plume," Atmos. Environ., (i press), 1979.

Goksoyr, H. and K. Ross, "The Determination of Sulfur Trioxide in Flu Gases," J. Inst. Fuel, 35, 177-179, 1962.

O'Neal, A. J., "Research Into Opacity Control at Northport, Long Islar Lighting Company," Internal Report, November 1978.

U. S. Environmental Protection Agency, "Standards of Performance fc Stationary Sources," Federal Register, 41(111), pp. 23076-85, Jur 1976.

Although power plant emissions of sulfur oxides amount to about two-thirds of total estimated emissions in the eastern United States, it is important to consider the budget and cycle of these emissions in the context of the total emissions of all related species. Sources of these other emissions include biological activity, industrial and commercial establishments, refineries, and automobiles and other forms of transport.

The relative importance of emissions from biological activity is a matter of considerable scientific debate. Altshuller (1976) maintains that the very low $SO_4^=$ concentrations that can occur at non-urban sites indicate that natural emissions play a minor role in the regional sulfur budget. Hitchcock (1977), however, has suggested that swamps and marshes can be important sources under some temperature and precipitation conditions. Supported by some limited observational evidence, and apparently consistent regional and seasonal patterns of airborne concentrations of sulfates and nitrates, Hitchcock concludes that the bacteriogenic hydrogen sulfide is an important source of atmospheric particulate matter. Critics respond that although patterns may be consistent, and on a world-wide basis such emissions may be important, that in the eastern United States, natural sources are overwhelmed by anthropogenic emissions that also undergo processes giving airborne concentrations consistent with observations (Galloway and Whelpdale, 1979).

EPRI and EPA are both supporting research to investigate the matter further. As part of EPRI's effort, Washington State University researchers are making measurements over different types of soil, plants, water bodies, swamps, and marshes throughout the eastern United States (at least in one case with the cooperation of a MAP3S researcher). Early indications are that the amount of emissions can be extremely variable from place to place, but that total emissions are considerably less than anthropogenic emissions.

In planning the MAP3S program, the tacit assumption was made that biogenic emissions could be neglected, an assumption based in part on a modeling study by Meyers and Cederwall (1975) showing that even with an upper estimate of biogenic emissions, resulting concentrations would be on the order of only 1 μg/m^3 along the northeast coast and less elsewhere in the eastern United States. The focus instead was on developing a regional inventory of emissions from anthropogenic sources (Benkovitz, 1978), recognizing that data on biogenic emissions might later need to be included if research of others found it to be important.

4.1 DEVELOPING A REGIONAL EMISSIONS INVENTORY

In developing a regional inventory of non-power production emissions, the initial estimates came from the NEDS inventory, as has already been described in Section 3.2. This inventory includes data on both point and area sources of emissions. The point source data are computerized in a single inventory that identifies each point source by source type.

Table 4.1 illustrates the distribution in time of record of the point source data in terms of the number of point sources updated per year. Although almost half of the source emissions data are more than three years out-of-date (1977 and 1978 will be the verification period), the emissions of many of these sources are generally small in comparison to the power plant emissions that have been more recently updated. However, it is striking that the "1977 NEDS inventory" is not really a 1977 emissions inventory, but rather an inventory of all sources for which EPA has records in 1977. It will be very difficult to estimate the potential error that this will introduce into model verification studies.

Table 4.1 also provides an indication of the complexity of the problem. With more than 84000 sources (and there is little indication that all sources are reported in all of the states), the potential exists for many local air quality problems. MAP3S, however, is attempting to focus on regional impacts of all of these sources. This is not to indicate that local problems may not be important and are not deserving of study, but rather that the collective impacts of all these sources may also be important and need extensive development of scientific capabilities to be properly considered.

Cursory examination of the available source emissions data has indicated that considerable care must be taken before using them in verification studies. When the initial data are received, a number of data validation checks are performed as the points are considered for inclusion in the inventory. These include:

1.   Validity of state/county codes are checked.

2.   Point coordinates are checked for "rectangle window" of state.

3.   Operating schedules are checked for consistency.

4.   A check is made that the method of estimating emissions is specified for all non-zero emissions.

State/Line	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	UP Known	State Total
Alabama						225	97	73	107	256	136	32		925
Connecticut				1		477								478
Delaware				87	520	5		11	253	479	31	23		603
Florida	19				2113	831	463	358	58	791	403			3041
Georgia						117	436	19	30	2	989			1271
Illinois					25		89	110		4	1916			2808
Indiana					4	61	844	42	1530	24	1	865		3564
Kentucky			3		4	744	422	525	11	4400	2			5850
Maine			22		152	633	275	80	111	58	181			1591
Maryland			9	38	84			255	122			1	1	1418
Massachusetts				160	539	73	716	258	170	1				1917
Michigan					390		38	50	30	436	290			2452
Mississippi			10	10	359	601	1547	12	320	66		28		3585
New Hampshire					103	10	298	4	71	66	4			546
New Jersey					198	152	24	64	286	378	3073	1		4034
New York	4	19	105	215	50	1817	282	362	2738	9720	1617	7588		22852
North Carolina					504		1139	822	259	66	2212	405		4607
Ohio					6					2265				4888
Pennsylvania				2	1366	2685	99	389	134	1				4675
Rhode Island								452	148					602
South Carolina				9	319	225	296	203	79	169	74			1365
Tennessee					154	191	936	861	779	2221	1406		1	6558
Vermont							60	8	106	616	5			681
Virginia					3		1669	4		21	5			1804
Washington, DC							5			69	5		1	90
West Virginia						786	73	66	12	1003			1	1004
Wisconsin										27	45			1009
Year Totals	23	19	149	522	6891	9633	10174	5029	7368	23073	12389	8944	4	84218

for the long range transport models of the type being developed for the MAP3S program. Therefore, the first updating task concentrated on attempting to assign logical coordinates to all non-located major sources, where, in the first pass, a major source was defined as a source emitting at least 5×10^6 kg/yr of SO_2.

A number of redundancies in the source listing exist that can be used to determine source location. One of the items in the NEDS data, for example, is a SAROAD[*] city code for each plant. These codes correspond to a disaggregation level similar to the U. S. Bureau of the Census MED-X[**] place code. MED-X data include the latitude/longitude of the population centroids for political and statistical subdivisions down to the enumeration district and block group. Computerized matching to locate a point source is done using these two possible parameters:

1. If available, SAROAD city code/MED-X place code.

2. Place name in plant address/MED-X place name.

If the computerized search fails, hand matching is attempted.

To implement the above described location format the following ancillary files were obtained or developed:

1. SAROAD/FIPS[+] state-county codes correspondence (obtained from EPA via Lawrence Berkeley Laboratory).

2. SAROAD city/MED-X place codes correspondence.

3. Latitude/longitude data for state and county outlines (obtained from Lawrence Berkeley Laboratory).

4. ZIP code/state-county-MED-X place correspondence file (recently obtained from Oak Ridge National Laboratory). The ZIP code file is in the process of being incorporated into the location criteria.

To further quality check the locations of point sources computerized procedures are being developed to test the relationship of

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[*]SAROAD = Storage and Retrieval of Aerometric Data (EPA).

[**]MED-X = Expanded Master Enumeration District List.

[+]FIPS = Federal Information Processing Standards.

Table 4.2 presents the initial results of efforts to provide location coordinates for sources for which data were not available in the NEDS data base. Figure 4.1 shows the location of the 200 largest SO_2 emitters in our current point source inventory. The NEDS inventory also includes

TABLE 4.2. Results of Coordinate Updating Task.

State Name	No. Plants	No. of Points	Updated Coord.*	Missing Coord.
Alabama	395	925	61	96
Connecticut	153	478	0	2
Delaware	137	603	2	29
Florida	1232	3041	146	446
Georgia	303	1271	11	23
Illinois	699	2808	44	87
Indiana	1501	3564	79	159
Kentucky	1802	5850	22	55
Maine	657	1591	12	106
Maryland	214	1418	2	2
Massachusetts	1098	1917	1	58
Michigan	1048	2452	390	431
Mississippi	1699	3585	13	1403
New Hampshire	301	546	0	6
New Jersey	663	4034	0	98
New York	5844	22852	22	220
North Carolina	2056	4607	296	874
Ohio	1243	4888	3	16
Pennsylvania	1566	4675	39	191
Rhode Island	262	602	0	24
South Carolina	524	1365	63	95
Tennessee	2203	6558	722	777
Vermont	185	681	1	13
Virginia	664	1804	3	18
Washington, D.C.	31	90	0	2
West Virginia	313	1004	4	17
Wisconsin	309	1009	29	33
TOTALS	27102	84218	1965	5274
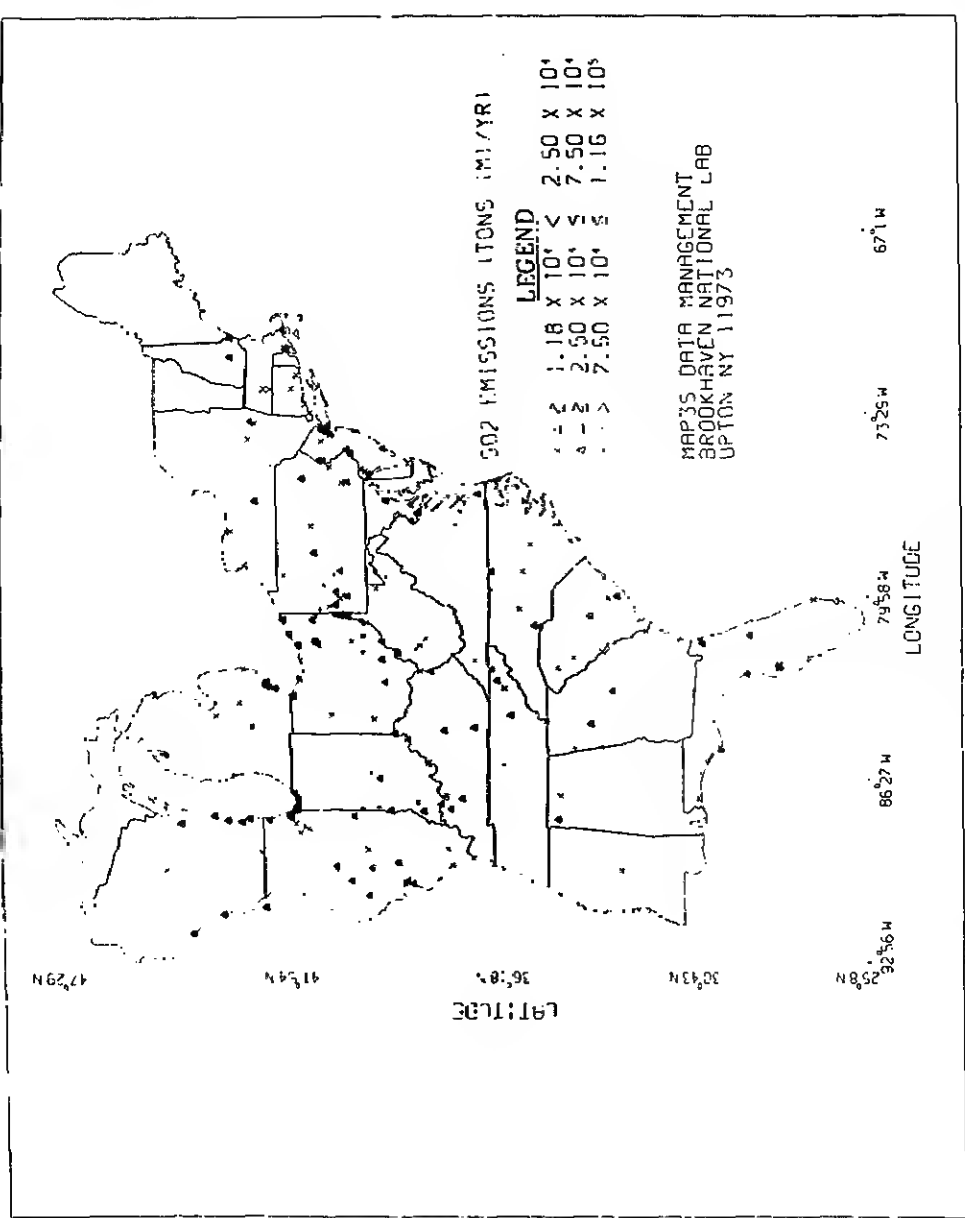
FIGURE 4.1 Location and emissions magnitude of the 200 largest SO₂ emitting sources (including power plants) in the eastern United States, as given in

agglomerations of such individually small sources as automobiles, residential and small commercial heating units, etc. Initial scan of the area source emissions data obtained from NEDS showed no data had been received for several states. Contact with local agencies resulted in partial data being received for the State of New York; gridded data received for the State of Rhode Island; and a gridded inventory on magnetic tape received for the State of Connecticut. New York data had to be added to the data base by hand since the data were not computerized; the computerized Rhode Island data can be used directly when manipulated with grid-to-grid transformation procedures; the Connecticut data were unusable due to inconsistent and missing information.

Table 4.3, 4.4 and 4.5 present the current totals for emissions of the five criteria pollutants as included in the MAP3S inventory. Table 4.5 presents emissions by major category within the Standard Industrial Classification code system. This table was compiled for a parallel study that required the inclusion of emissions data for the state of Puerto Rico.

Initial contact has been established with the Air Quality and Meteorology Section of the Ministry of Environment for the province of Ontario, Canada. During 1978, data for point source and area source inventories were received. These data are currently being studied and, if feasible, will be reformatted and converted into data bases compatible with the MAP3S inventory. To the best of our knowledge, no other compiled Canadian emissions data are available.

Efforts to upgrade the inventory are in progress, by, for example, assuring that the computerized data bases always contain the most up-to-date data available. In order to provide the MAP3S modeling community with a "base emissions inventory," procedures to "checkpoint" the inventory data are being developed (Benkovitz and Evans, 1978). A data subset suitable for modeling runs will be extracted from the data

TABLE 4.3 MAP3S Emissions Inventory for 27 States.

| | Emissions (10^6 tonnes/yr) | | | | |
	Particles	SO$_2$	NO$_x$	HC	CO
Point Sources	6.00	20.73	7.44	2.47	9.10
Area Sources	3.04	3.07	7.19	10.50	50.74

TABLE 4.4 MAP3S Point Source Emissions Inventory

	No. of Plants	No. of Points	Emissions (10^3 tonnes/yr)				
			Particles	SO_2	NO_x	HC	CO
Alabama	395	925	122	214	68.6	71.7	57.
Connecticut	153	478	22.5	111	39.8	15.3	7.0
Delaware	137	603	21.6	169	22.0	18.1	8.
District of Columbia	31	90	2.1	7.9	4.7	.7	3.
Florida	1232	3041	160	993	478	39.0	79.2
Georgia	303	1271	74.6	538	174	9.0	108
Georgia	699	2808	764	2290	1390	410	458
Illinois	1501	3564	408	1820	1190	141	1590
Indiana	1802	5850	564	1500	321	189	68.
Kentucky	657	1591	34.7	108	29.0	48.2	54.
Maine	214	1418	59.3	470	136	46.2	106
Maryland	1098	1917	52.8	239	75.5	79.1	32.
Massachusetts	1048	2452	300	1490	400	211	492
Michigan	1699	3585	142	125	69.5	42.8	205
Mississippi	301	546	10.6	94.3	35.3	41.1	21.
New Hampshire	663	4034	54.7	311	192	254	190
New Jersey	5844	2852	229	422	229	66.4	68.
New York	2056	4607	194	433	184	50.6	124
North Carolina	1243	4888	867	3180	573	180	2420
Ohio	1566	4675	758	2700	598	113	276
Pennsylvania	262	602	2.2	10.9	5.6	17.3	2.
Rhode Island	524	1365	107	268	128	41.9	122
South Carolina	2203	6558	311	1150	277	97.1	180
Tennessee	185	681	.7	.7	.3	1.7	.
Vermont	664	1804	348	419	160	111	195
Virginia							

TABLE ... emissions inventory by
Standard Industrial Classification (SIC)*

			Emissions (10^3 tonnes/yr)			
SIC Code	SIC Category	No. of Plants	Particles	SO_2	NO_x	HC
0000-0999	Agriculture	1835	164	1565	374	31
1000-1999	Mining	1008	483	87	9	47
2000-2999	Manufacturing	8495	1183	2326	738	1316
3000-3999	Manufacturing	7338	2030	1753	754	755
4000-4999	Transportation, Electric and Gas Service	2420	2105	14878	5510	189
5000-5999	Trade	1352	34	31	12	144
6000-6999	Finance	688	1	7	3	0.3
7000-7999	Services	548	0.7	5	2	4
8000-8999	Services	3013	39	84	30	2
9000-9999	Public Administration	652	42	131	44	27

*As taken from "Standard Industrial Classification Manual 1972," Executive Office
President, Office of Management and Budget.

d of the current location update cycle and inclusion of corrections entified by the EPRI/SURE contractor (GCA, Incorporated). Other neckpoints will be taken as experience and user requests dictate.

Future development work is being planned in the following areas:

1. EPRI's Sulfate Regional Experiment (SURE) program is also supporting work to develop a comprehensive emissions inventory (Corbin et al., 1978). Exchange of information is taking place between BNL and the SURE emissions inventory contractor, GCA/Technology Division. To date, the exchanges have involved listings of the corrections each group has found are needed in the NEDS inventory, with our efforts focusing on location corrections, and GCA's efforts focusing on corrections based on engineering consistency checks. We are independently evaluating these corrections and expect to include them in our revised inventory. GCA is also developing seasonal, three hourly emissions data for all power plants in the eastern United States that should allow the two programs to develop the most comprehensive emissions inventory yet available for modeling, verification, and policy evaluation studies.

2. Quality checks of data already in the inventory will be extended. Items to be checked include stack parameters, material and energy data, emissions and fuel data.

3. Periodic extraction of current NEDS data is scheduled. Updates and changes in these data will be evaluated and incorporated in the MAP3S inventory.

4. Area source data will be scanned for completeness. Additional sources of such data and/or procedures for data development will be searched for and explored.

5. To facilitate input of source emissions data to atmospheric models, cooperative efforts with MAP3S modeling groups will be extended as a means of developing more appropriate computer procedures for data preparation.

Altshuller, A. P., "Regional Transport and Transformation of Sulfur Dioxide to Sulfates in the U.S.," J. Air Pollut. Control Assoc., 26, 318-324, 1976.

Benkovitz, C. M. and V. A. Evans, "User Access to the Source Emissions Inventory," MAP3S memo, July 1978.

Benkovitz, C. M., "Compiling a Multistate Emissions Inventory," presented at the Special Conference on Emission Inventories and Factors, APCA-TP7 Committee, Anaheim, CA, November 1978.

Corbin, V., R. Hall, and N. F. Surprenant, "Emissions Inventory in the SURE Region," Quarterly Progress Report No. 3, GCA/Technology Division, Bedford, MA, July 1978.

Galloway, J. N. and D. M. Whelpdale, "An Atmospheric Sulfur Budget for Eastern North America," submitted to Atmos. Environ., 1979.

Hitchcock, D. R., Biogenic Sulfur Sources and Air Quality in the United States, Final report to NSF-RANN, Arthur D. Little, Inc., Cambridge, MA, 1977.

Meyers, R. E. and R. T. Cederwall, "Fossil Pollutant Transport Model Development," in Annual Report for Fiscal Year 1975, BNL Regional Energy Studies Program, BNL-50478, 1975.

The careful identification of pollutants found in the atmosphere is essential to adequate understanding of the role played by emissions from power plants and to determining the toxicity of the emissions. Directly emitted gaseous pollutants (e.g., SO_2, NO_x) have been sampled for many years. They have been followed out to tens of kilometers downwind from power plants. They are reasonably well characterized and, in most cases, have been controlled to such an extent that air quality standards developed by EPA are being met. For secondary, or derivative, compounds (e.g., ammonium sulfate and bisulfate, sulfuric acid mist, sulfite, etc.) there are very few measurements, most observations have reflected only the total suspended particulate and/or sulfate burden. Relatively few sophisticated analyses have looked at such properties as molecular form, particle size distribution (usually, sulfur is found in particles smaller than 0.5 μm), acid sulfate speciation, oxidation state, associated cations, etc. In the cases of total sulfate burden and specific species concentrations, researchers have had to consider the possibility of pollutant transformation in the collection instrument or on the filter. It may be such uncertainties and the limited amount of high-quality information that are causing poor correlations between atmospheric concentrations and health effects in community health studies.

For these reasons MAP3S is devoting considerable effort to developing more accurate measurement techniques of airborne concentrations of particles, including both their chemical composition and their physical form. Our work in these areas is described in sections 5.1 and 5.2. The instruments described in these sections have been used in a number of characterization and field studies described later in this report.

Pollutants are also found in precipitation, and understanding of the budget and paths of the energy-related emissions requires knowledge of the pollutant concentration in rain and snow. Measurement and analysis techniques of precipitation have been a focus of research groups within DOE and its predecessors for many years. This expertise, developed because of interest in radionuclide scavenging, has been largely redirected to focus on emissions from fossil-fuel combustion. Section 5.3 describes the analysis techniques being used to sample and analyze precipitation samples. The network established to collect samples and some of the preliminary results from these studies are described in Chapter 6.

5.1.1 Real-Time Measurement of Aerosol Sulfate and Sulfuric Acid

The attainment of the MAP3S goal of "characterization of physical and chemical properties of AER pollutants" is exceptionally difficult with respect to aerosol sulfur quantification and speciation from filter sample data alone, even with cooperative data exchange with the SURE program. The need for real-time aerosol sulfur measurement capability was considered so vital to the MAP3S goal that substantive effort has been expended at BNL in developing a flame photometric detection (FPD) system for use in both ground and airborne measurements. This effort has been aided substantially, especially in regard to the pressure response calibration of the Meloy FPD sulfur analyzer, by interaction with the airborne measurements group at PNL within MAP3S and with Husar and his colleagues at Washington University, through the STATE program.

Measurements of aerosol sulfur following removal of gaseous sulfur compounds in a diffusion-denuder tube upstream from the FPD have been reported by Coburn et al. (1978) and Huntzicker et al. (1978), using a new commercially available FPD with exceptionally low noise (< 2 ppb). Several factors limit the utility of the reported systems: response to environmental variables such as relative humidity, barometric pressure and CO_2 concentration; electronic peculiarities of the FPD logarithmic amplification scheme; response variability with burner temperature; and difficulties of instrument calibration with aerosol sulfates of differing composition at ambient levels.

As part of MAP3S, a system has been devised for ambient aerosol sulfur measurement (Tanner et al., 1978a) using an FPD sulfur analyzer with a heated denuder to remove SO_2. Cyclic addition of ammonia permits discrimination between sulfuric acid and other sulfate aerosols while eliminating the reduced system response to sulfuric acid. During ammonia addition all aerosol sulfate is measured whereas the heated denuder volatilizes and removes sulfuric acid aerosol when no NH_3 is added. The effects of water vapor and pressure changes on the zero level and sulfur response of the FPD burner response have been studied in detail. Applications of this real-time system (see Fig. 5.1) to ground measurements of ambient aerosol sulfur at dynamically varying relative humidity and to airborne measurements at variable barometric pressure are now possible if the system is carefully and frequently zeroed.

An experiment using an FPD-based real-time sulfate measurement system calibrated with aerosol sulfate was conducted at BNL in July 1978, and the data are presented in Fig. 5.2. Aerosol sulfate data are
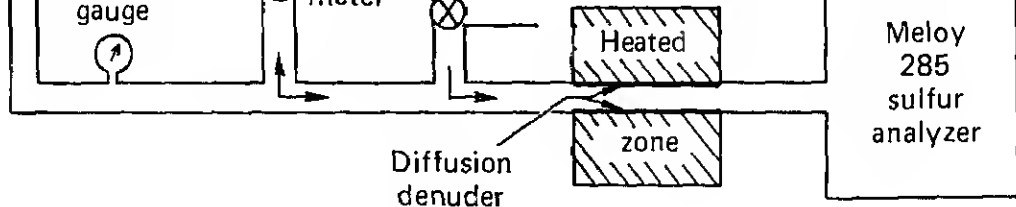
(a) Ambient sampling system
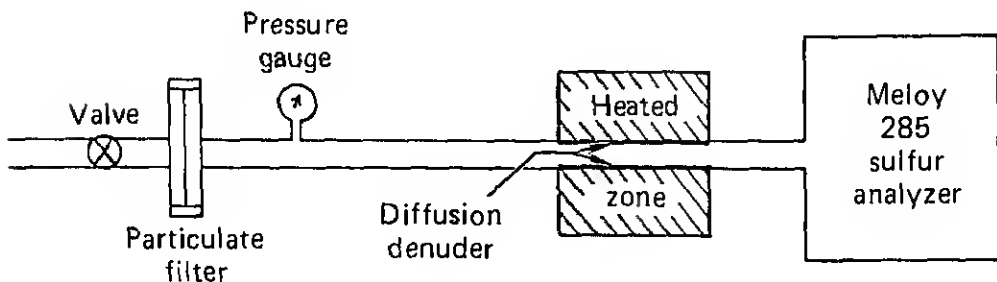
(b) Zeroing system

FIGURE 5.1 Schematic diagram of real-time aerosol sulfate/sulfuric acid monitor developed by BNL for MAP3S.

even when strong acid levels (as measured by Gran titration of filter samples) were high on 22-23 July. The sensitivity and specificity of the system to as little as 0.5 ppb aerosol sulfur has thus been demonstrated when proper adjustment has been made for electronic abberations of the commercial linearized amplification system.

Modifications to this system are being made with the following objectives: (a) development of an automatically zeroing, real-time sulfur system for ground-based measurements with post-collection correction of data for relative humidity changes; and (b) implementation of an airborne real-time sulfate monitor with post-collection correction of
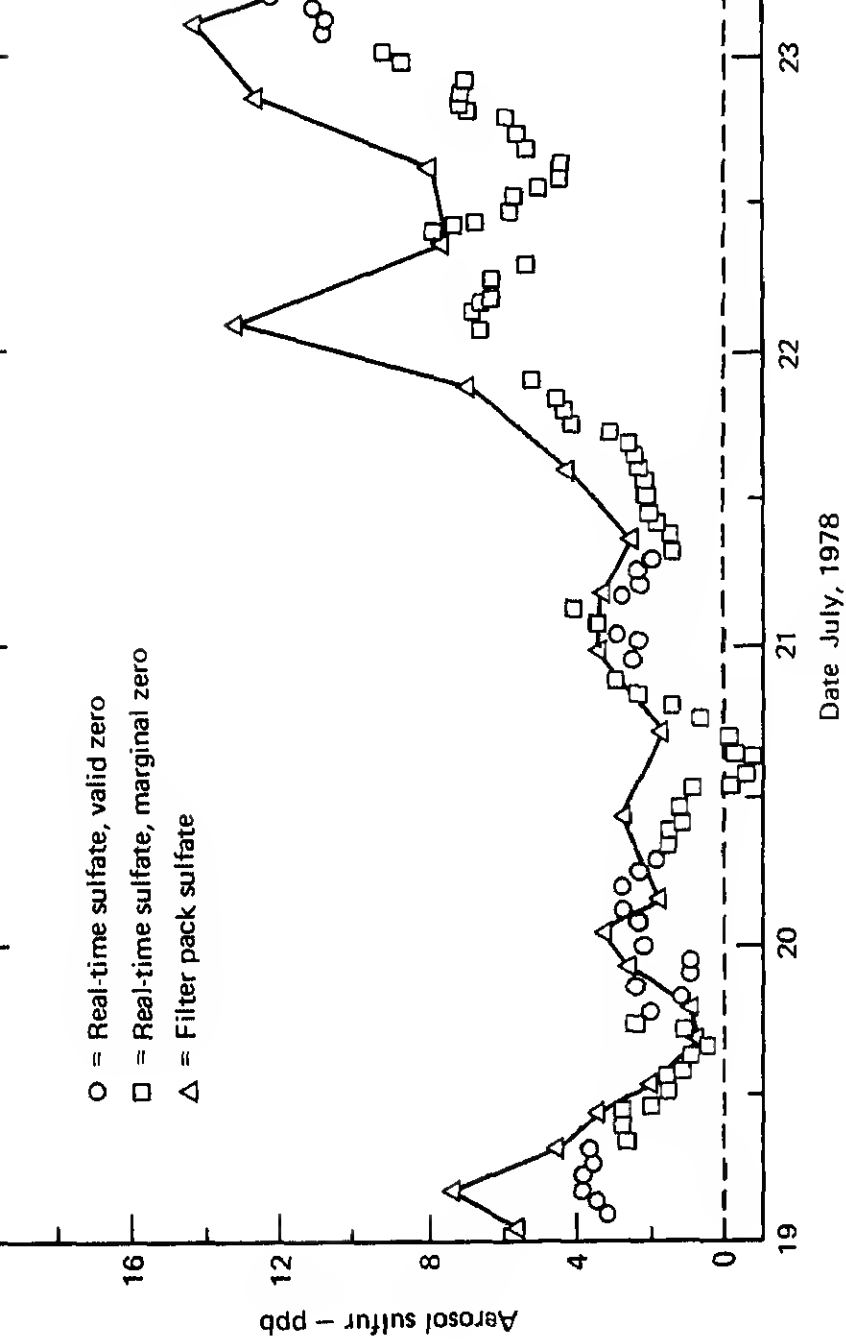
FIGURE 5.2 Aerosol sulfur as measured by real-time flame-photometric detector (FPD) a...

O = Real-time sulfate, valid zero

□ = Real-time sulfate, marginal zero

△ = Filter pack sulfate

Date July, 1978

Aerosol sulfur — ppb

necessary for successfully conducting large "box-budget" experiments on a sub-regional scale.

A separate effort in sulfur and sulfate sensing has resulted from the need for highly sensitive and rapidly responding detectors for use in micrometeorological studies at ANL. After initial tests of commercial flame photometric instruments in early 1977, the need for special instrumentation became apparent. A much faster responding instrument is presently under development at the University of Michigan,[*] intended for application in the ANL studies of dry deposition. However it is anticipated that this new, water cooled flame photometric sensor will have wider application, especially in aircraft operations.

5.1.2 Other Developments for Determination of Aerosol Sulfur and Precursor Compounds

5.1.2.1 Analysis of S(IV) and Other Reduced Sulfur Compounds

Calorimetric analytical procedures have been developed in part in conjunction with the MAP3S program by Eatough et al. (1978a) at Brigham Young University for the analysis of metal-sulfite and organo-sulfite complexes in aerosol samples. Whereas inorganic S(IV) concentrations are usually less than 15% of sulfate, it appears that the organic-S(IV) species may vary from a negligible fraction of the sulfur content to nearly 50% of the sulfate level depending on the aerosol source, acidity and sample age. Independent ion chromatographic and West-Gaeke analysis techniques were found not suitable for analysis of S(IV) species in aerosol samples. Analytical techniques based on volatilization of SO_2 from the samples or extraction into benzaldehyde have been developed for analysis of the organic S(IV) species and will be used in conjunction with the calorimetric procedure in future sampling programs. Photoelectron spectroscopy is also being routinely used to compare surface to bulk concentrations in collected samples (Eatough et al., 1978a, 1979).

Results of experiments performed in a smelter plume where the collected sample was chemically "fixed" at the sampling site immediately after collection and where the sample was returned to the lab for normal analysis clearly indicate that inorganic S(IV) is lost from

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[*]The University of Michigan sulfur sensor development program is separately funded by DOE; ozone and NO_x sensors are also being developed. The Michigan project is under the leadership of Dr. D. H. Stedman.

aerosols containing the organic adduct. To test this hypothesis samples were collected and analyzed on site in summer, 1978, at the EPRI SURE sites at Rockport, IN and Duncan Falls, OH and at a MAP3S site at State College, PA. The acidity of the collected aerosol varied from neutral at Rockport to highly acidic at State College but organic-S(IV) species were routinely seen at all sites. Results of stored sample analysis will determine a sampling protocol to be recommended for routine analysis of S(IV) species in the MAP3S region.

The possible loss or chemical conversion of volatile or reactive sulfur containing species during x-ray fluorescence (XRF) analysis and the relative sensitivity of the technique to sulfur in reduced oxidation states has been examined. The importance of these effects is suggested by the sample analyses shown in Table 5.1. It has been shown that the low values obtained by x-ray fluorescence techniques (e.g., PIXE) as reflected in these results is due to the loss of volatile compounds (i.e., H_2SO_4) and irradiation induced loss of reactive species (S-IV) (Hansen et al., 1979).

5.1.2.2 Measurement of Sulfate and Related Species in Collected Aerosol Samples

Acquisition of a sulfate data base suitable for MAP3S objectives is in no small measure the result of advancing knowledge of appropriate procedures for sampling and analysis of aerosol sulfate. It is now established that Teflon and acid-treated quartz filters do not catalyze the in situ oxidation of SO_2 to "artifact" sulfate, whereas glass fiber filters commonly used in other sampling networks do produce artifact sulfate in varying degrees. Teflon-coated glass filters (as used in the SURE sampling network) apparently produce negligible artifact sulfate for 24-hr sampling but are marginally inert for shorter sampling periods. The phosphoric acid-treated tissue quartz filters developed at BNL are to be preferred for high volume sampling with the inert Teflon filters preferred for low volume applications.

Analysis techniques for sulfate in aerosol samples are suitably precise, accurate and sensitive for most MAP3S needs as shown by the results of the EPA/ERDA Intercomparison Study held in Charleston, WV in May, 1977 (Camp et al., 1978). Agreement between sulfate determinations was ± 16% of the mean of all determinations. The preferred technique for aqueous sulfate is now ion chromatography, principally due to its sensitivity and freedom from interferences although Methylthymol blue (MTB) colorimetry is adequate for many applications. Techniques which are waning in importance due to inadequate sensitivity or interference problems include turbidimetry, flash volatilization-FPD,

TABLE 5.1. Comparison of PIXE Results for Total Sulfur with Wet Chemical Results for Total Sulfate.

Sample	Pretreatment for PIXE	PIXE Total S as $SO_4^=$, wt%	Total $SO_4^=$+S(IV), wt% by:	
			Calorimetry	I.C.*
Coal power plant fly ash	H_2O or HCl extracts	0.6	1.3	1.0
Oil power plant fly ash-1	HCl extracts	25.0	45.0	-
Oil power plant fly ash-2	HCl extracts	7.0	13.0	-
Smelter plume highly acidic	None	15.0	47.0	40.0
$HOCH_2SO_3Na$	Various	6.17	24.0	24.0

*I.C. = Ion Chromatography.

sulfate after collection and oxidative extraction from carbonate-glycerol impregnated cellulose filters. It is also frequently used by both the BNL and BYU groups to determine particulate sulfate extracted from aerosol samples collected on quartz filters, and particulate metal sulfates in flue gas samples. IC has now replaced the flash volatilization-flame photometric technique for determination of sulfate in samples resulting from extraction of sulfuric acid from quartz filters by benzaldehyde. Benzoic acid is an interferent in this procedure; it may be removed by thermal pre-treatment under conditions where no sulfate is lost.

Some samples have also been simultaneously analyzed for nitrate and sulfate using IC. Analysis conditions used are relatively standard except for prefiltration of aqueous extracts and the addition of a pre-column to protect the principal anion separator column from soluble organics.

Automated analyses for sulfate by MTB colorimetry and other soluble ions in aerosols are routinely performed by the BNL group using a dual channel, modular Autoanalyzer II recently interfaced to a programmable calculator for automated readout of sample concentrations. Modifications in sample preparation, including prefiltration and ion exchange cleanup, allow determination of sulfate to 0.5 µg/ml but blank variability with quartz filters reduces the effective sensitivity somewhat.

An interesting observation made in early MAP3S-related experiments at BNL and confirmed by the EPA/ERDA Intercomparison Study was the agreement between total sulfur measurements principally by physical methods (XRF, PIXE) and sulfate measurements by extraction and wet chemical techniques. Data from the intercomparison study show a sulfate/sulfur mass ratio of 3.03 ± 0.34 which is indistinguishable from the stoichiometric value of 3.00 (Camp et al., 1977). This contrasts with the data of the BYU group (Eatough et al., 1978a) who report frequent, significant levels of S(IV) species. Future work within MAP3S should ascertain whether differences in results are due solely to transformations during sample storage and/or extraction or if other effects such as sample loss during PIXE or XRF analysis should be implicated.

Analysis of strong acid by Gran titration as developed by Brosset et al. at the Swedish Water and Air Pollution Research Laboratory and modified at BNL is in a high state of development, and both H^+ and ammonium determinations (the latter by indophenol colorimetry) on aqueous extracts of airborne particles may routinely be made (Tanner et al., 1977).

Infrared spectroscopy is being used by the Environmental Chemistry

collected on each of the 4 impactor stages and shipped to ANL for analysis. Preparation of the samples for Fourier-transform infrared spectroscopy consists of milling the collected particulate matter with potassium bromide and pressing this mixture into a pellet.

To facilitate processing of the infrared spectra for the large number of samples being analyzed, a computer program has been developed to perform the interpretation and ion quantification. Analysis is routinely performed on every fifth sample from stage IV (nominally 0.3 to 1.0 µm aerodynamic diameter particles) and on other selected samples from stage IV and stage III (1.0 to 3.0 µm aerodynamic diameter particles). All remaining samples from stages III and IV, along with the after filters, are stored under dry nitrogen for possible future analysis. Quantitative results are obtained for the ammonium, nitrate and neutral sulfate ions. Qualitative results are obtained for acidic sulfate and other sample constituents.

Development of solvent extraction techniques for speciation of sulfur (VI) compounds in airborne particles, especially the use of benzaldehyde and isopropanol for selective extraction of sulfuric acid and bisulfate, respectively, from aerosols containing other sulfates, has continued at BNL. Additional MAP3S-related work on the benzaldehyde/sulfuric acid technique has been done at BYU and supplemented by EPA- and CRC-funded work at Southern Research Institute and Rockwell International, respectively. It has been shown that sulfuric acid in amounts as low as 5-10 µg may be extracted with reproducible, high efficiency from Teflon or treated quartz filters without interference from ammonium or metal sulfates that also may be present. Efforts to use benzaldehyde extraction results together with ammonium, strong acid, sulfate and nitrate data to obtain ion balances that would shed light on the homogeneity of ambient aerosol sulfate composition, have met with mixed results.

Eatough et al. (1978b) have reported that benzaldehyde may extract significant quantities of bivalent metal bisulfates. If contaminated with benzoic acid, it may extract metal-sulfate complexes or even ammonium bisulfate (Richards et al., 1978), in contrast to earlier reports (Tanner et al., 1977). Metal bisulfates and sulfite complexes are unlikely to be abundant in ambient aerosols but additional work is in progress to clarify the specificity limitations of the technique with respect to ammonium salts. The benzaldehyde extraction method is limited by the tediously lengthy procedures required and by the interference of benzaldehyde and benzoic acid with many sulfate analysis techniques. However, since the extraction methods are more nearly specific than other techniques and

5.1.3 Measurement of Other AER Pollutants

5.1.3.1 Nitrate, Nitric Acid

The determination of nitrate in aerosol samples has been performed as a part of the MAP3S characterization task because aerosol nitrates are the presumed end products of photochemically active atmospheres into which nitric oxide is emitted. The role of nitric acid in the "smog" cycle involving various nitrogen oxide compounds has been suspected but measurements have been, until recently, difficult to perform and the data sparse.

Measurement of aerosol nitrate in aqueous extracts of MAP3S airborne particulate samples has been performed using the automated reduction-colorimetric technique and in some cases by ion chromatographic analyses. Results from internal comparison at BNL and from the EPA/ERDA Intercomparison Study demonstrate equivalency of these methods. However, several studies have now shown that nitrate results by differing sampling media are not equivalent (Camp et al., 1977; Stevens et al., 1978). Ten-fold elevated nitrate levels on glass relative to Teflon filters have been reported and attributed to collection of gaseous nitric acid by the former and not by the latter. However, alternate explanations involving post-collection reactions of acidic sulfate and nitrate aerosols also have some merit. It is extremely important to the MAP3S characterization effort that sampling methodologies be improved, tested, and intercompared so the modified procedures for accurate measurement of particulate nitrate may rapidly be implemented.

Recognition of the need for specific, routine measurement of nitric acid vapor at ambient levels has recently evolved within both the MAP3S and EPA research communities, due both to particulate nitrate sampling difficulties and to negative correlations observed between acidic sulfate and particulate nitrate levels. Sodium chloride-impregnated cellulose filters have been shown by Forrest et al. (1979) at BNL to collect HNO_3 vapor at 90+% efficiency downstream from treated quartz prefilters in a high volume sampler. No adsorption of NO_2 on the NaCl-impregnated filters with retention as nitrate was observed. Conversion of NO_2 to nitrate or released HNO_3 on the prefilter was negligible. Adsorption of nitric acid on the quartz prefilter was significant at high humidities (e.g. 18% of 2 ppb HNO_3 adsorbed at 85% RH), but the HNO_3 could be removed by brief post-collection sampling of dry, clean air. Ambient levels of HNO_3 in the range of 0.7 to 6 ppb were observed which constituted 60-90% of the total gaseous and particulate nitrate. The

capture detection. The use of Teflon prefilters limits the sampling rate, but this is compensated for by the extreme sensitivity of the analytical method. In fact, using a modification of the nitro-derivatization method developed independent of MAP3S support by Tanner et al. (1978b), HNO_3 at 0.5 ppb may be easily determined with 5 minute time resolution in ambient samples. If the nylon filter medium proves adequate, the derivatization method may have advantages making it preferable for use in future field sampling experiments.

Alternate schemes for measuring nitric acid continuously using an NO/NO_x chemiluminescence instrument as reported by Joseph and Spicer (1978) are promising but difficult to implement in practice. The potentially quantitative interference of HNO_3 and peroxyacetylnitrate (PAN) with NO/NO_2 measurements by chemiluminescence should in fact be studied more thoroughly in the future.

Surface measurements of gaseous NO/NO_x, ozone, total and nonmethane hydrocarbons, and SO_2 have been made sporadically by the BNL group in conjunction with MAP3S and SURE sampling periods. A few measurements of gaseous hydrochloric acid were made utilizing the carbonate/glycerol filters which were also collecting SO_2 downstream from a particulate prefilter. The analytical method is a colorimetric method involving release of thiocyanate by chloride from its aqueous mercuric complex.

5.1.3.2 Carbonaceous Aerosols, Miscellaenous

In addition to sulfur and nitrogen particulate species, the ambient aerosol has a large carbonaceous fraction which, in general, is a complex mix of organics and elemental carbon. Although MAP3S has focused primarily on the impacts on visibility of sulfur and nitrogen compounds, there have been indications that the carbonaceous component of particles may also be playing a role. Of particular concern is the characterization of the ambient carbonaceous aerosol in terms of its primary (produced directly from combustion) and secondary (produced by atmospheric reactions) components. Such characterization is essential if meaningful control strategies are to be devised. For this purpose LBL has developed a technique using the high optical absorptivity of urban aerosols as a tracer for primary emissions. During the past year, this technique has yielded some significant results for samples collected in two California air basins and at Argonne National Laboratory, near Chicago. The technique is based on the fact that the high optical absorptivity or black coloration of ambient and source particulate samples is due to the "graphitic" carbon component (Rosen et al., 1977, 1978), which can only be produced directly from high temperature

1. The optical attenuation of the particles collected by the Millipore substrate. This is a measure of the blackness of the samples and should be proportional to the "graphitic" soot content.

2. The total carbon content of the particles determined by combustion of the quartz fiber filters.

Ambient aerosol samples have been collected daily since 1 June 1977 at LBL, Berkeley, California; since 15 July 1977, at the Bay Area monitoring station in Fremont, California; and since 19 August 1977, at the South Coast monitoring station in Anaheim, California. Samples were also taken from 23 March 1978 to 9 April 1978 at Argonne, Illinois. A number of representative sources have been sampled. About 100 analyses have been made of the following particulate emissions: (1) exhaust collected in a freeway tunnel under conditions of moving traffic with few diesel trucks; (2) automobile exhaust collected in an underground parking garage under start-stop driving conditions with no diesel trucks; (3) exhaust from a small 2-stroke engine; (4) exhaust from a small 4-stroke diesel engine; and (5) stack samples from a natural-gas-fired domestic water heater. Figure 5.3 shows optical attenuation vs. carbon loading for the samples collected at Berkeley, Fremont, Anaheim, and Argonne. All of the graphs have the same scale of axes, enabling direct comparison and determination of the following very important results:

1. There is a strong correlation ($r \approx 0.85$) between optical attenuation and total suspended particulate carbon mass at every site.

2. The mean specific attenuation, i.e., the coefficient of this proportionality, is virtually identical at each site.

Figure 5.4 shows the distribution of specific attenuation (ratio of optical attenuation to total carbon content) of ambient samples from all sites taken together, subdivided according to peak hour ozone concentration. Clearly, there is little trend for high-ozone days to be characterized by aerosols of strongly diluted attenuation. Furthermore, the maximum correlation coefficients of peak-hour ozone concentration and specific attenuation at any individual site or all samples taken together are $r = 0.24$ and $r = 0.11$ respectively. This places a rather low limit on the maximum importance of secondary carbonaceous particulates formed in ozone-indicated atmospheric reactions.

Similar measurements made on particulate matter emitted directly
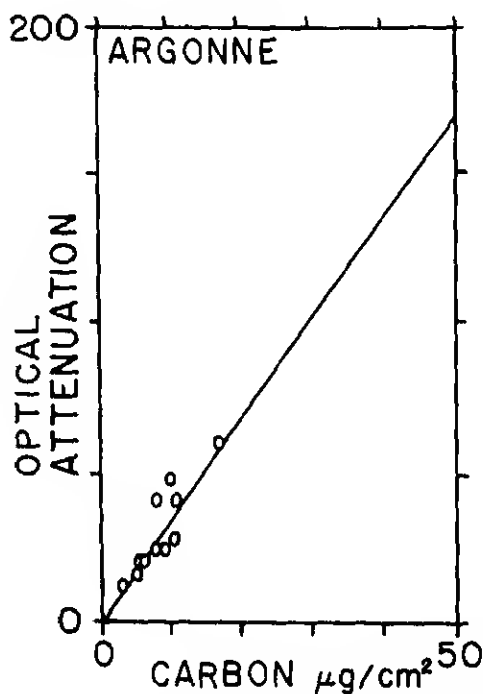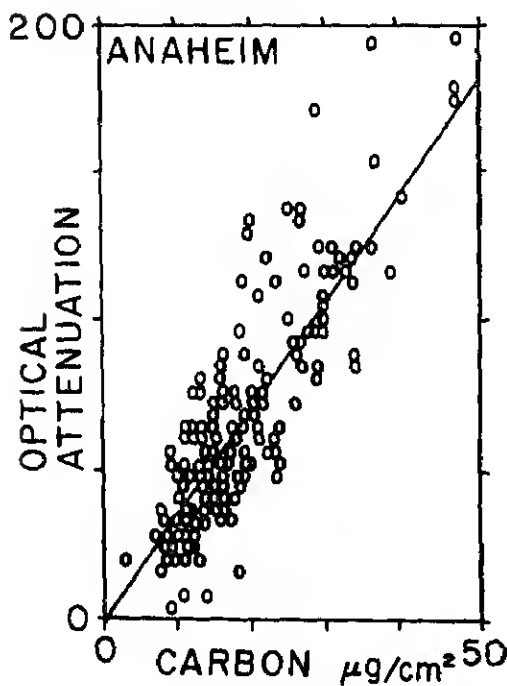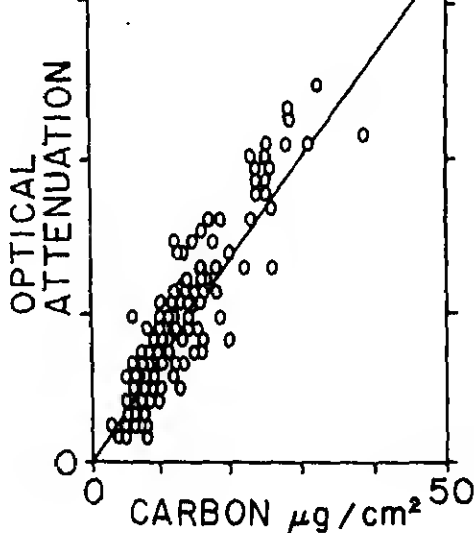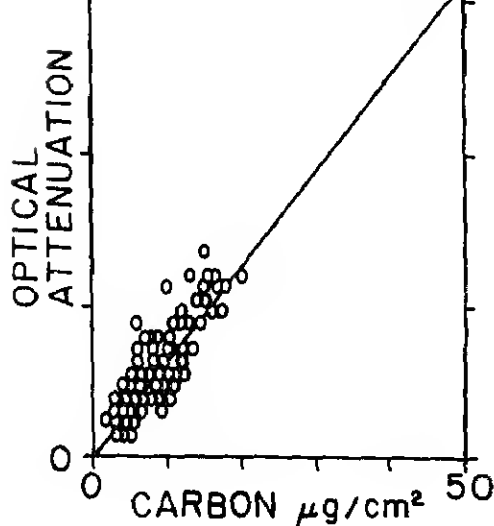
FIGURE 5.3 Optical attenuation vs. particulate carbon loading for ambient samples collected at Berkeley, Fremont, Anaheim, and Argonne. Least-squares fit line is shown.

(a) peak ozone < 75 ppb
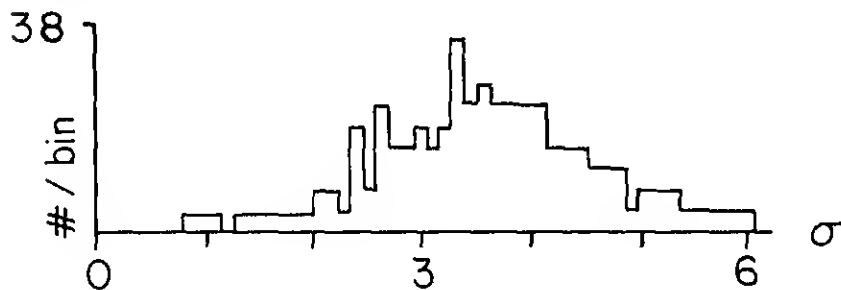
(b) peak ozone > 75 ppb
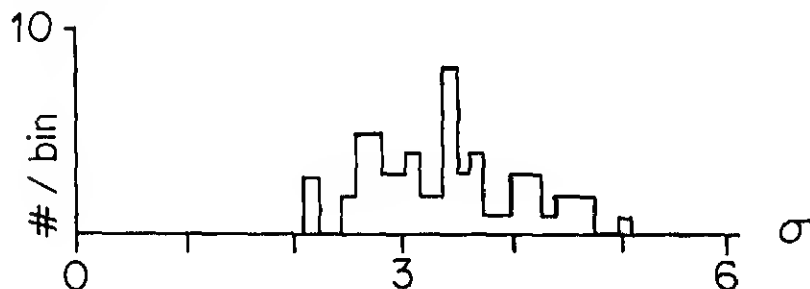
FIGURE 5.4 Distribution of values of specific attenuation of the ambient particulate samples, subdivided according to peak hour ozone concentration. The specific attenuation, σ, is defined as the ratio of the optical attenuation to the total carbon loading per unit area and should be proportional to the fraction of the carbon in "graphitic" form.

content that is comparable to that found in ambient samples. These results strongly suggest that a major fraction-possibly the dominant fraction-of the carbonaceous aerosol burden at these sites is due to primary emissions.

Future measurements in later stages of MAP3S should probably incorporate more detailed characterization of carbon-containing constituents of ambient aerosols. Such data are needed to further investigate the role of aerosol carbon compounds and their relation to

heterogeneous S(IV)-S(VI) conversion processes. The existing methods for differentiating between volatilizable and graphitic carbon, that are being optimized by the LBL and BNL groups and others should be included in future experiments. Research in developing simple and rapid methods for functional group quantification of atmospheric organics in both gaseous and aerosol form should also be encouraged.

Selected use of methods for nitrous acid, hydrogen peroxide and other organic peroxyacids in some future field experiments now seems both feasible and desirable.

5.1.4 Interprogram Comparison of Filter Analysis

Because of the importance of assuring that valid data are being gathered, an interprogram comparison of filter analyses has been initiated between the MAP3S and SURE programs. As part of this effort, Environmental Research Technology, Inc. (ERT) has exchanged laboratory reference solutions and duplicate aerosol filters with the Environmental Measurements Laboratory (EML) of the Department of Energy. Both ERT's Concord Laboratory in Massachusetts, which performs most of the routine analyses of the SURE samples, and its Westlake Village Laboratory in California, which is responsible for the internal quality assurance of ERT, participated in these exchanges.

Reasonable agreement among the laboratories was obtained from the analyses of the reference solutions. Linear correlations were made between EML's results and those of the ERT laboratories for reference solutions with concentrations that ranged from about 1/100 to equal to what would be expected from exposed filters. Compositing the results from both ERT laboratories, a -7% bias was observed from EML's results for $SO_4^=$ and -12% bias for NO_3^- over this concentration range. Only the Westlake Laboratory reported NH_4^+ results which reflected a +8% bias from EML's data. Generally, the percent deviation among the laboratories decreased with increasing concentration. However, another set of reference solutions, which reached three orders of magnitude higher concentrations, still reflected a negative bias of about 5% for both $SO_4^=$ and NO_3^-.

Fractions of the same total aerosol filters were analyzed by the Concord Laboratory and EML as duplicate samples for $SO_4^=$, NO_3^- and NH_4^+. Preliminary results indicate good agreement for $SO_4^=$ (within ± 5%). Comparison of results for the other species is still pending.

As a second part of the interprogram comparison, BNL has provided specifically pre-treated filters for use in the SURE aircraft program. These filters provide a time integrated measure of SO_2 concentrations

integrated method also allows measurement to very
because of the extended averaging time. At present, including quality
control filters, analyses have been performed on about 200 filters from
SURE aircraft flights. Because the MAP3S aircraft are also equipped for
this sampling technique, data collected by the combined set of
MAP3S/SURE aircraft during intensive periods should be intercomparable.

A similar comparison has recently been initiated at several SURE
ground stations. About 80 filters have been analyzed to date.
Comparison with data from continuous gas samplers is in progress.

5.2 METHODS FOR PHYSICAL CHARACTERIZATION OF AEROSOLS

Four interrelated lines of activity contributing to the measurement of
aerosol physical properties have been pursued under MAP3S. These
include:

- Development of new or improved equipment for the measure-
  ment of aerosol properties.

- Analysis of submicron aerosol size distributions.

- Size distribution interpretation of size-separated, chemically
  characterized aerosol samples.

- Investigations of the physical bases of aerosol measurement
  methodology.

These areas are discussed in the following sub-sections.

5.2.1 Measurement of Physical Aerosol Properties
A special-purpose size-discriminatory aerosol sampler was designed
and constructed for use on the MAP3S Islander aircraft. The device was
intended to provide a capability to sample both power plant plumes and
the regional background aerosol. The sampler's isokinetic sampling probe
and aerosol conduit leading to the plane's interior and a two-stage, 200
l.p.m. dichotomous virtual impactor with a fifty percent penetration
diameter of under 2000 nm, are located outside the cabin. The
approximately 175 l.p.m. small-particle flow from the dichotomous
virtual impactor is directed to a slit-to-cylinder impactor with a 500 nm
fifty percent penetration diameter. The remaining small particles then
pass through a "honeycomb structure" diffusion processor with a nominal
fifty percent penetration diameter of 50 nm. Since a diffusion battery
fifty percent penetration diameter on regional

slit-to-cylinder impactor and following the honeycomb structure part of the diffusion processor. This system is currently being installed in the aircraft (see Fig. 5.5).

For ground-based aerosol sampling, an identical slit-to-cylinder impactor was constructed. It will be used with a screen-type diffusion processor of either one or two size cuts affording considerable versatility. A cloud condensation nuclei (CCN) counter identical to the airborne one is being acquired to be used with a diffusion battery for size distribution determination.
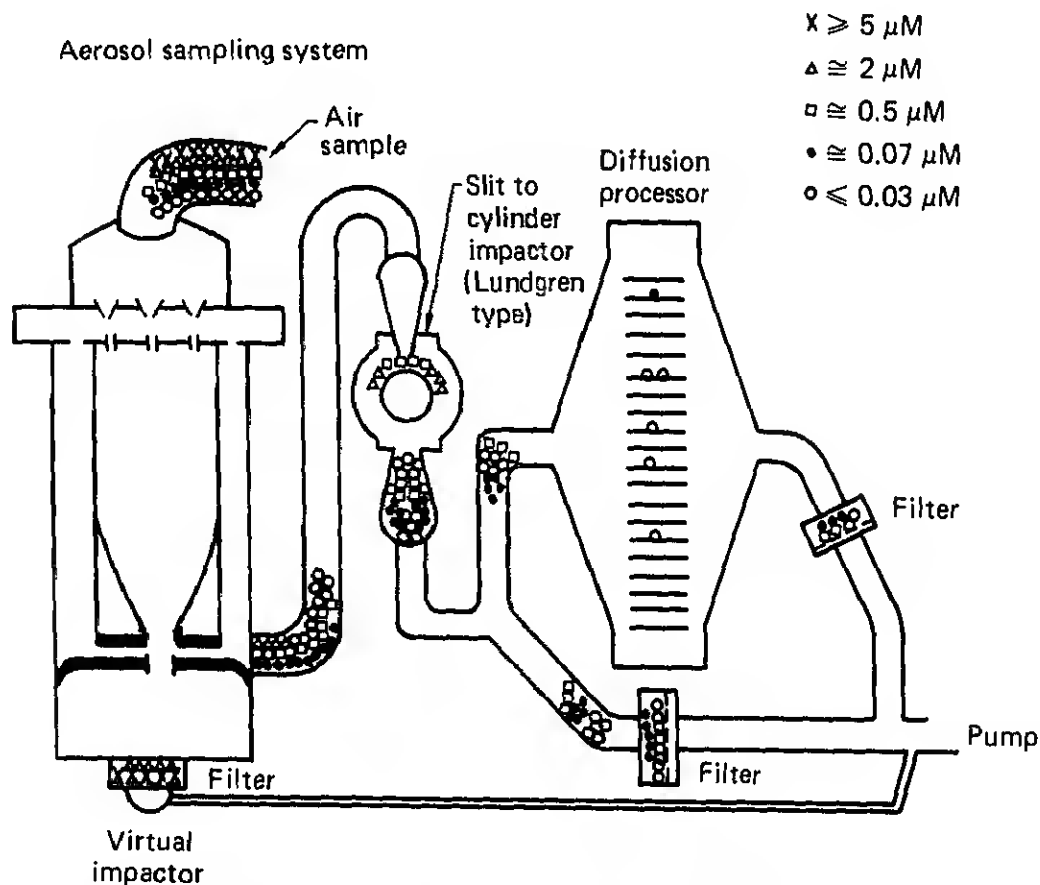
FIGURE 5.5 Schematic diagram of MAP3S airborne aerosol sampling system.

A rapid, very simple, curve-fitting routine was developed by EML and BNL to aid in analyzing aerosol size distributions. By employing a computational algorithm originally described by Twomey (1975), an aerosol instrument's measurements can be interpreted in terms of a polydisperse aerosol of discretely-sized particles via its monodisperse aerosol calibrations with no a priori assumptions on the shape of the distribution curve. The routine provides a common analytical procedure for the analysis of Electrical Aerosol Analyzer "EAA" (Thermo Systems, Inc., St. Paul, Minnesota) and diffusion battery data. This allows both rigorous intercomparison of the methods and merging of incomplete data sets, as was done for the 1976 New York Summer Aerosol Study (see Section 6.1). To complete the curve-fitting routine, appropriate statistical measures of goodness-of-fit that account for the uncertainties in the calibration curves will be incorporated. These should include the environmental influences upon the aerosol measurements that affect detection of the various size and composition particles in different ways.

5.2.3 Size Distribution of Aerosol Samples

Interpretation of data from diffusion-processed aerosol samples requires simultaneously measured size distributions for meaningful interpretation of the mass distribution of chemical species among the aerosol particles. Such data were taken in the 1976 New York Summer Aerosol Study where data from an EAA were used to interpret diffusion-processor derived samples and were also compared with intermittently available diffusion battery data. The complete diffusion processor data analysis allowed identification of size-dependence of aerosol sulfate species that contributed to the understanding of their origin and fate as discussed in Section 5.1.

A relatively small but possibly significant disagreement between diffusion battery and EAA generated aerosol size distributions during their common sampling period in the New York Summer Aerosol Study needs to be resolved to complete year-around sulfate measurement interpretation. Simultaneous winter size distribution measurements will be taken to help resolve this question, which arises from an approximately twenty percent aerosol volume difference in the calculated diffusion processor penetrations.

Conventionally, size-discriminatory, chemically characterized particle samples are taken during 6 to 24 hour sampling periods, time intervals far too long to observe important transients such as the "sunrise effect" for particle generation or the effect of weather frontal passage. The ground-based high volume aerosol sampler described above will be used in parallel with a diffusion battery capable of taking its full

particles larger than 100 nm can be reproducibly charged, and therefore, in principle, sized, whereas smaller particle charging is always influenced by the spectrum of the cluster ions and therefore inappropriate for detailed size distribution determination. These results mean that considerable variability in the distribution of particles under 100 nm inferred from such electrical measurements may be expected due solely to the variability of environmental trace gases rather than the aerosol itself (see Fig. 5.6).

Particle deposition on fibers or other surfaces is common to filtration and diffusion-based aerosol measurement methods as well as dry and wet deposition. Nevertheless, there is no framework in which aerosol and surface composition considerations can be incorporated to estimate the likelihood of particle-surface collisions and therefore removal of the particles from the air. Calculations will be performed to investigate what effect monolayer "oil" or electrolyte coatings of glass and teflon filter fibers will have on their ability to capture realistic atmospheric particles.

5.3 SAMPLING AND ANALYSIS OF PRECIPITATION CHEMISTRY

The importance of precipitation scavenging as a removal pathway for atmospheric pollutants is well known. The pollutant uptake by precipitation that results from this process can result in substantial modification of the chemical makeup of snow and rainwater. These changes in turn can drastically alter the chemical budgets of terrestrial and aquatic ecosystems, that act as receptors for this chemical burden (see, for example, Likens et al., 1977).

MAP3S is interested in the relationships between pollutant release and precipitation chemistry, particularly with regard to response to anticipated increases in future emissions. This involves not only the actual measurement of very small rainborne pollutant concentrations, but also assuring that precipitation is collected, stored, and analyzed in a valid and representative fashion.

The strategy for measurement of precipitation chemistry in the MAP3S region was developed during the early stages of the project. The detailed procedures for sampling and analysis were formulated through a process of meetings and correspondence among laboratory and university participants and other interested researchers. In some cases these procedures were tested in network operation. In this section, we describe the methodology being used to sample and analyze precipitation
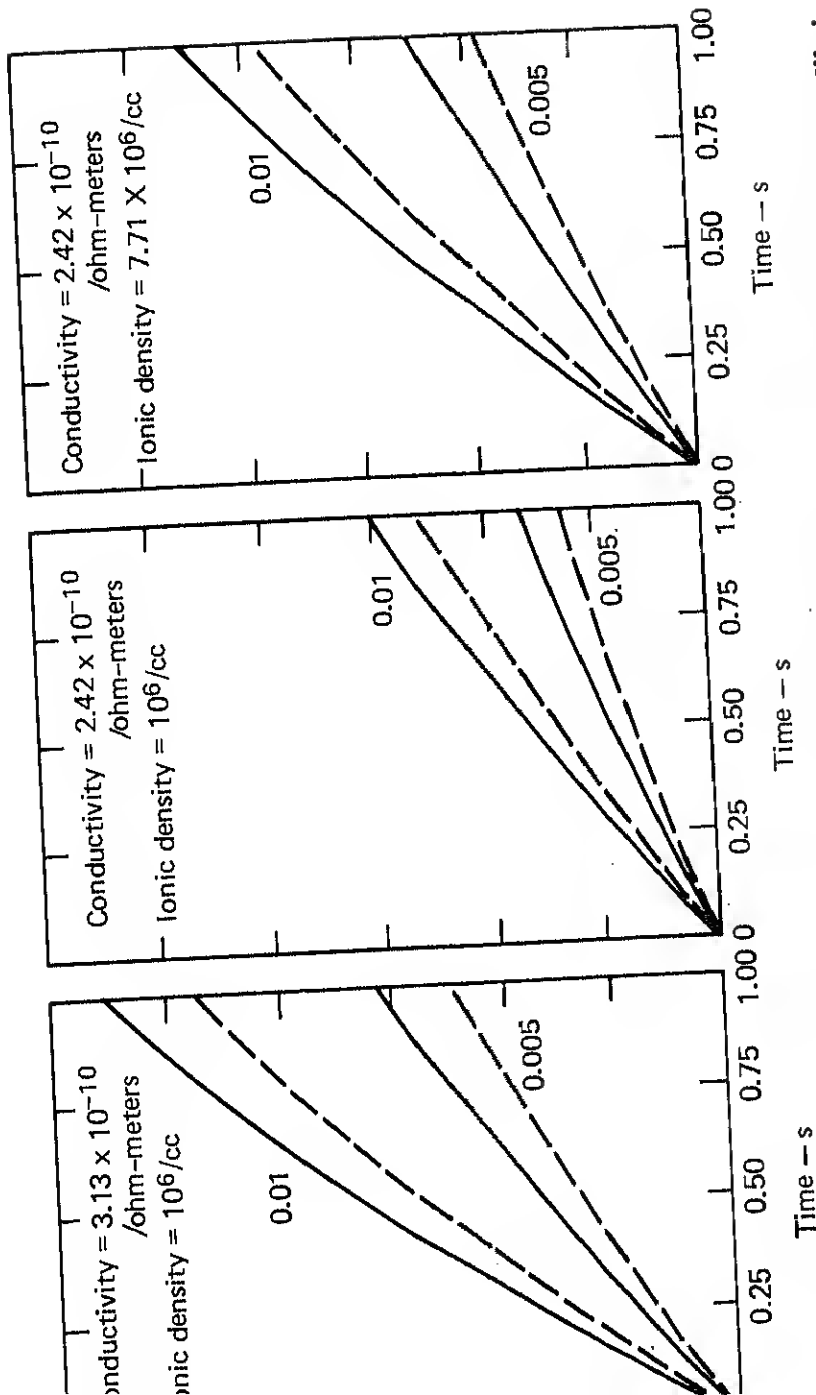
Figure 5.6 Average charge as a function of time. Numbers to right of lines are particle radii in micrometers. Solid and dashed lines respectively for particles with dielectric constants of 80 and 2. Graphs illustrate the ambiguity of the N_0t parameterization for transition and free-molecular regime particle charging if ionic mobility distribution is not fixed, as is the case in the environment.

methods may be found in the summary reports (1971, 1918) and associated publications (Hales and Dana, 1978).

The basic precipitation collector used in the network is a wet deposition-only type designed and constructed by Battelle Pacific Northwest Laboratory (shown in schematic form in Fig. 5.7). Two major features of this collector are different from other automatic precipitation samplers. First, a funnel and bottle collection scheme is used that allows for a relatively large exposed collection area. This scheme also provides for minimizing the splashing contamination hazard and the effects of turbulence from the collector structure, while maximizing protection of the collected sample from loss of volatile chemical constituents. Secondly, an enclosed chamber for storage of the collected sample is provided and is refrigerated during warm weather to minimize chemical changes that may occur at ambient temperature. This type of collector, which was largely untested prior to MAP3S network operations, was compared directly on an event sampling basis with the established Health and Safety Laboratory[*] (HASL) collector at four sites for approximately the first eight months of MAP3S network operation. The reliability and sample comparability of these two sampler types was about equal during this period. Since that time, the HASL collectors were devoted to special studies as described further below.

Precipitation sampling is conducted on a precipitation event hasis in order to provide a basis for later tracking back polluted air masses to source regions. For reasons of practicality, however, the normal minimum sample time is 24 hours with recovery of the collected sample accomplished as soon as possible after the conclusion of the event. Despite efforts to preserve and rapidly analyze precipitation samples, chemical changes can still occur. Thus, we initiate sample analysis efforts immediately upon sample collection. The operator of the sampler performs a pH measurement on an aliquot of the sample, and decants one 20 ml aliquot into a separate container. This latter aliquot is treated with sufficient tetrachloromercurate (TCM) to preserve dissolved SO_2 (sulfite).[+] A portion of the main sample is placed in one or two 250 ml polyethylene bottles and, along with the TCM aliquot, is refrigerated prior to shipment to the central chemical laboratory at PNL. Shipment

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[*]The HASL has been renamed the Environmental Measurements Laboratory, but the collector name has not changed.

[+]The terms "dissolved SO_2" and sulfite are used interchangeably in this report to denote all sulfur species in the aqueous phase in the IV valence state, including dissolved undissociated SO_2, bisulfite ion, and actual sulfite ($SO_3^=$) ion.
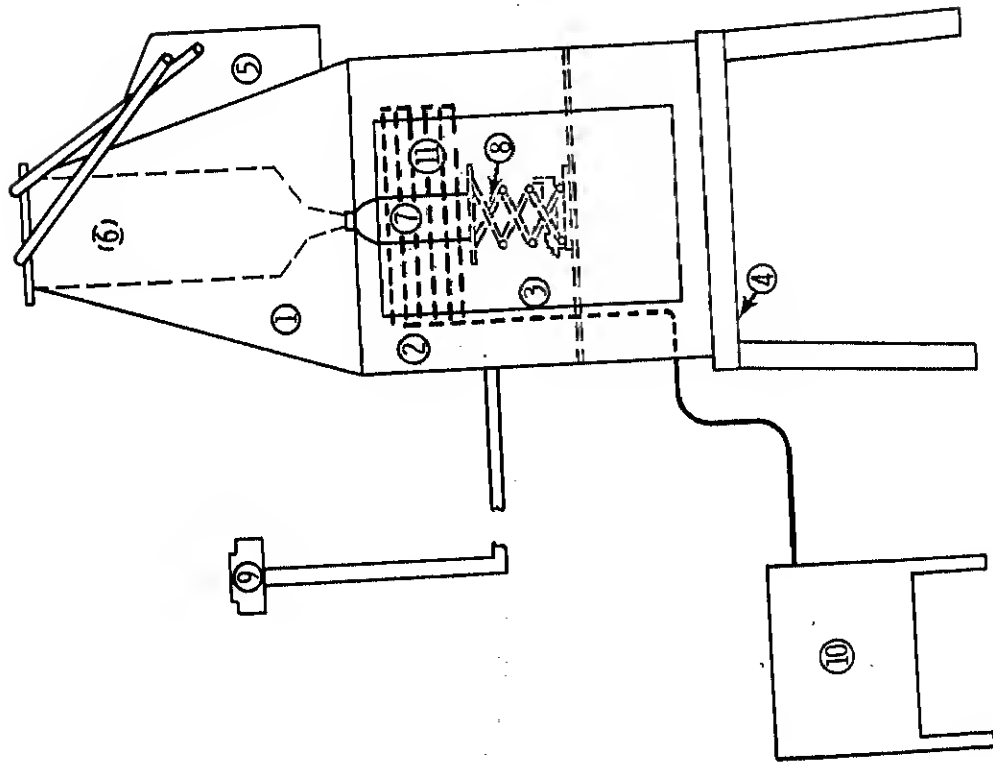
1. FIBERGLASS TOP SECTION
2. FIBERGLASS LOWER SECTION
3. ACCESS DOOR
4. ALUMINUM ANGLE BASE
5. MOTOR DRIVE SECTION
6. HEATED POLYETHYLENE FUNNEL
7. POLY COLLECTION BOTTLE
8. JACK TO SUPPORT SAMPLE
9. RAIN SENSOR UNIT
10. REFRIGERATOR UNIT
11. COOLING COILS

FIGURE 5.7 The PNL-designed precipitation collector used by the MAP3S precipitation

frozen and archived. Thus, the samples are maintained at low, but non-freezing temperatures from the time of collection to post-analysis freezing, except for a short period of time during shipment in the warmer months.

Preparation of the Battelle collector for the next event involves rinsing of the funnel with about 2 l of distilled, deionized (DD) water, and replacement of the 2 l collection bottle and the polyethylene collector lid cover that forms the seal between the lid and funnel during non-precipitation periods. The funnel rinse is collected, and is measured for pH and/or conductivity as a check for contamination.

The site operator keeps a detailed log of sample on and off times, volume, pH, and collector opening times, precipitation (from a standard rain gauge), and qualitative wind, storm type, and precipitation character information. These data are forwarded to PNL for eventual inclusion in data reports and the MAP3S data bank. Monthly data listings are also issued, with the lag time between sample collection and reporting averaging only two to three months.

The PNL Atmospheric Sciences Department chemical laboratory performs chemical analyses for the species listed on Table 5.2. Also shown are methods and minimum detectable concentrations. The basic laboratory instrument is the ion chromatograph (IC). Two such instruments are used to determine concentrations of the major ions: four from the anion unit and three from the cation unit. A large number of NH_4^+ analyses were performed by two methods during the changeover of cations from automated wet chemistry and atomic emission spectrophotometry to IC; the results compared favorably.

PNL participates in a multi-faceted quality control program. PNL took part in EML's intercomparison study, which involved blind analyses of standard precipitation samples by 23 laboratories. PNL compared favorably in its analysis capabilities (PNL is laboratory No. 11 in the preliminary report (Bogen et al., 1978). A formal laboratory control program has also been established, administered by EML as part of the network operation. EML instructs the network site operators to periodically include in sample shipments either duplicate samples or standard samples provided by EML. Realistic, but fictitious data accompany the samples, so that all network project personnel at PNL are blind to sample identity. A disinterested quality control officer at PNL removes and, through communication with EML, reidentifies quality control samples prior to their inclusion in data reports. In addition, internal, non-blind, duplicate analyses of samples are also reported.

Species	Method*	Instrument	Minimum Limit micromoles/l
H^+ (free)	Electrode	Orion 801A, Combination Electrode	-
Conductivity	Bridge	Beckman RC-16C Bridge, Yellow-Springs 3403 Cell	-
$SO_3^=$	AWC	Technicon Auto Analyzer	0.1
$SO_4^=$	IC	Dionex System 10 (Anion)	0.2
NO_2^-	AWC	Technicon Auto Analyzer	0.05
NO_3^-	IC	Dionex System 10 (Anion)	0.2
Cl^-	IC	Dionex System 10 (Anion)	2.0
PO_4^{3-}	IC	Dionex System 10 (Anion)	0.2
NH_4^+	IC	Dionex System 10 (Cation)	0.6
Na^+	IC	Dionex System 10 (Cation)	0.4
K^+	IC	Dionex System 10 (Cation)	0.25
Ca^{++}	AA	Perkin-Elmer 306	0.25
Mg^{++}	AA	Perkin-Elmer 306	0.4

*AWC = Automated Wet Chemistry; IC = Ion Chromatography; AA = Atomic Absorption Spectrophotometry.

water before shipment to the sites. Collector funnels and other permanent sample-contact items are cleaned with 6N HCl and DD water.

In addition to the routine chemical analysis of samples and data reporting, PNL and the network operators have undertaken several special studies to examine areas of uncertainty. Studies to date have been in four categories: (1) study of the role of dissolved SO_2 in wet deposition of sulfur; (2) preservation of volatile or transitory species; (3) comparison of sampling effectiveness of various types of collectors; and (4) investigation of sample stability when solid particles are present.

Dissolved sulfur dioxide has never before been adequately measured in samples from regional precipitation chemistry networks. It has been assumed that SO_2 scavenging was insignificant regionally because of reduced solubility of SO_2 in acidic precipitation, and because of relatively low SO_2 levels in the ground-level air. To test this assumption, MAP3S initiated a special study to determine the extent of SO_2 scavenging. In the fall of 1977 special treatment of sample aliquots with TCM to preserve sulfite was begun. Sulfite analyses were performed and the results compared with "total sulfur".[*] Figure 5.8 shows the resulting ratios of monthly mean deposition-weighted concentrations (MMDWC) for data from three sites with complete records through the winter season. The sulfite concentrations are relatively high during the cooler months, as one would predict from data on SO_2 solubility, which is increased as temperature decreases and pH increases. The magnitude of the sulfite concentrations is still quite low, however, since overall MMDWC for total sulfur are low in the winter (about 10 μmoles/l).

Studies of the preservation of sulfite and nitrite in DD water and precipitation samples indicated that these transitory species are sensitive to the conditions under which the samples are stored. The sulfite experiments that were done to establish sulfite analysis procedures for the network indicated that sulfite decays (oxidizes) very rapidly at room temperature, less so at refrigerator or freezer temperature, but still at a rate that requires chemical fixing with TCM at each site upon sample collection. By contrast, the nitrite ion is very stable in solution, with little decay at room temperature over periods of weeks. Only under freezing and thawing conditions does nitrite oxidize rapidly to nitrate. These results, along with the observed very low nitrite concentrations in network samples in all seasons, suggest that

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[*]Since, in untreated samples, sulfite oxidizes rapidly to sulfate, the measured sulfate concentrations measured in untreated samples are
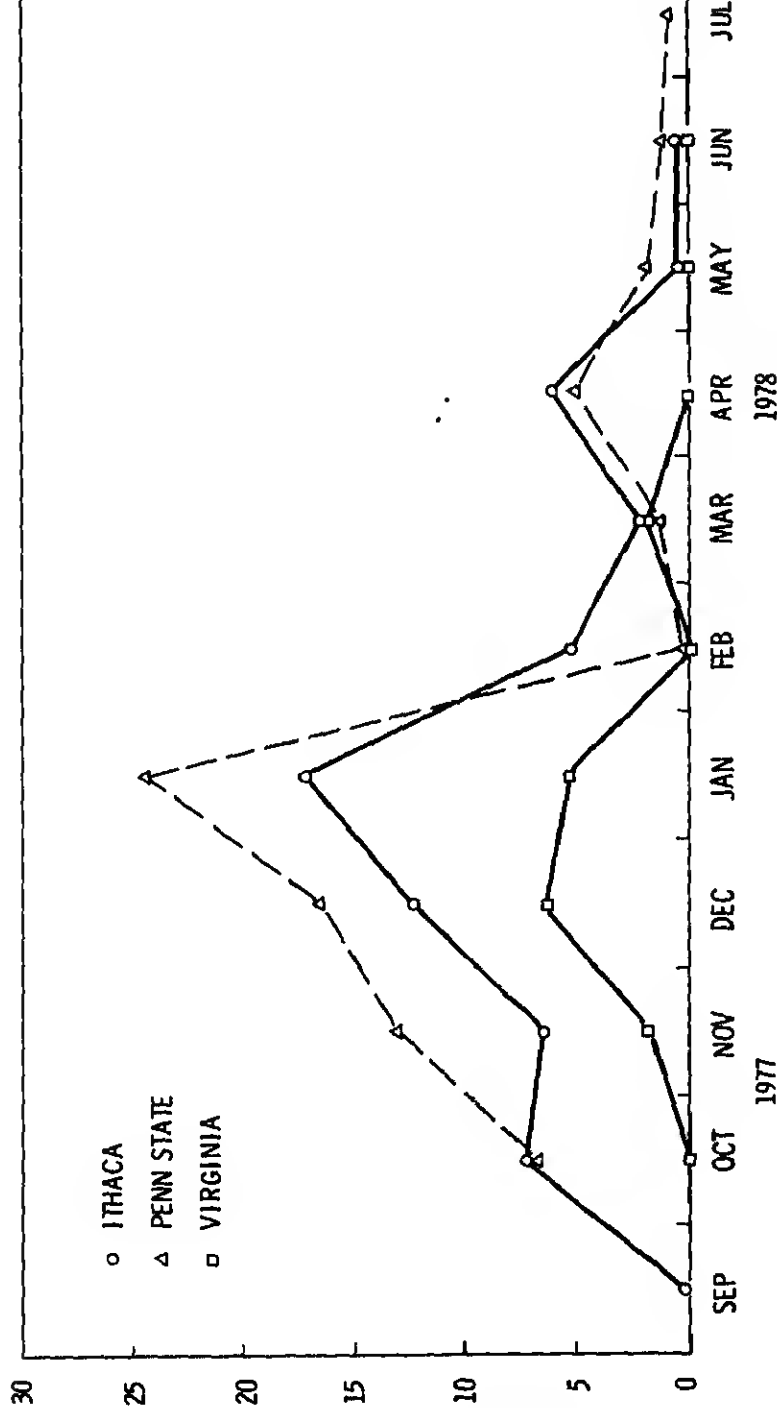
FIGURE 5.8 The ratio of monthly deposition-weighted averages of sulfite and total sulfur for three network sites.

Several collector comparison studies have been conducted in conjunction with network operations. The PNL and HASL collectors were compared on event sampling at four sites, with the result that for the major species ($SO_4^=$, H^+, NO_3^-, HN_4^+) these two collectors were found to sample nearly identically. For $SO_3^=$, monthly average concentrations are similar, but significant differences for individual events seem to occur for reasons which are hard to determine because of a lack of SO_2 air concentration measurements.

The effectiveness of the DD water rinse of the PNL collector after each sample was tested by running two PNL collectors at one site, operated identically except that with one its funnel was returned to the local laboratory and washed with HCl between samples. The concentrations obtained from samples taken with these two collectors compared favorably in limited testing. The integrity of PNL funnels was also tested by performing complete analyses on rinse from each funnel for the first few months of operation. These indicated that little error should result from neglect of the quality of pollutant species removed in the rinse on samples of volume greater than about 100 ml. Limited testing with double rinses indicated that the 2 1 rinse is probably adequate in removing the major species (H^+, $SO_4^=$, NO_3^-).

Several of these special studies are also being pursued as part of a more comprehensive collector intercomparison study underway at the Pennsylvania State University site. Three each of three types of collectors are being operated on an event sampling basis.* The third type of collector (in addition to the PNL and HASL-type) is that used by the Canadian Atmospheric Environment Service network (CANSAP) in their monthly sampling program. The HASL-type collector is being used for weekly sampling as part of the recently initiated National Atmospheric Deposition Program NC-141 network and the EPRI event sampling network. The study is being cooperatively supervised by researchers from the several participating groups, and data are being exchanged. Results from this special study will help provide the basis for comparing data being collected by the four major networks in North America. SO_2 air concentrations are being monitored during this study to help determine collector differences for dissolved SO_2 sampling, and to test the concept of equilibrium scavenging of SO_2. All chemical analyses except for sulfite are being conducted at PNL. This study began in mid-May 1978. Initial results will be evaluated further in the spring of 1979.

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*Subsequent studies are being considered using various sampling periods.

comparison with PNL collectors on an event sampling basis, and then utilized for sulfite measurements only, were placed in weekly sampling mode in June 1978. These measurements should help in determining if weekly sampling is adequate for precipitation chemistry monitoring purposes, as is now underway as part of the NC-141 project, the focus of which is on monitoring total chemical inputs to the surface rather than providing data that will allow sources of the pollution to be identified.

Finally, the ISWS has examined the variations of ions in precipitation samples for various combinations of sample handling and sample storage methods. The results indicate that solid particles should be removed from precipitation samples and the filtrate acidified to insure valid analytical results (Peden and Skowron, 1978). This finding will be evaluated as part of continuing review of the procedures being used in the network collection of samples.

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Although federal, state, and local agencies, and commercial groups, support programs to monitor pollutant concentrations, at the start of MAP3S existing data on air quality and precipitation chemistry were inadequate to permit either verification of numerical models or investigation of important transport, transformation and deposition processes. The most extensive set of data on particulate sulfur concentrations, for example, was probably that of the National Air Sampling Network (NASN), which included only a 24-hr sample taken every 12th day. A utility-sponsored network analysis by Hidy et al. (1976) had daily data available, but over a domain more limited than the MAP3S region. Both sets of data pointed to the general location of elevated sulfate levels, but they were unable to provide clear evidence for either long-range transport or local pollutant deposition. Nor could the data sets be used to identify such specific subregional phenomena as river valley pollutant plumes and the relative influence of local and regional emissions. Measurements of the vertical pollutant distribution were even more sparse than those of the horizontal distribution. Consequently, circumstances could not be identified that led to such phenomena as the trapping of pollutants aloft by the nocturnal inversion, probably an important element in the long-range transport of pollutants.

Available data also did not adequately represent the variation in time of energy related pollutants, nor did they identify local sources that may unduly influence individual observations. Pollutant peaks lasting only several hours and multiday episodes may occur, yet without proper time resolution such events can be missed or poorly represented by a sampling network, thereby making the assessment of health and ecological effects difficult, if not impossible. To complicate matters further, toxicological and ecological studies have not yet resolved the relative effects of short, intense dose and long, low-level doses. Until such identification is done, measurements must cover temporal variations as fine as a few hours.

A greatly improved data base, describing the present concentrations of pollutants in air and precipitation in terms of average and extreme conditions, was a recognized need of the MAP3S and SURE programs. Such a data base is needed to provide insight into the spatial extent of elevated pollutant levels, the regional coherence of polluted air masses, the selection of "episode" cases for model verification studies, and the data necessary for testing various hypotheses of sulfate transport and transformation. EPRI, assisted by its utility members, focused the SURE program on the development of an extensive network of surface stations: 9 highly equipped stations, operating continuously beginning in August 1977, and 45 lesser-equipped stations, operating during month-long intensive periods each season between August 1977 and

Rather than duplicate the extensive air quality measurement program planned as part of SURE, MAP3S chose to pursue a three pronged approach to further expand the data base so that it would be adequate for the needed studies. These three parts included:

- Augment the SURE surface air quality network with a network that would measure aerosol properties in more detail than SURE[*];

- Utilize aircraft to measure pollutant concentrations above the surface, the horizontal and vertical extent of and, where possible to coordinate with the SURE aircraft program to provide more extensive coverage;

- Develop a regional precipitation chemistry network to sample on an "event" basis and to gather the data needed to relate emissions to pollutant concentrations in rain and snow.

In this chapter we describe the progress made on these three tasks as part of MAP3S. This description does not include a discussion of the results from the SURE program that are now becoming available (Mueller et al., 1979), and so does not present a full description of our knowledge of the region's air and precipitation quality. The SURE data are, however, being included in the MAP3S data bank (see Section 13.1) and will be available for evaluation and analysis as part of MAP3S studies.

6.1 SURFACE MEASUREMENTS

The MAP3S surface measurement activities include the analysis of fine particles collected by two relatively limited networks of non-urban stations across the MAP3S region (one to measure aerosol acidity, one to measure aerosol composition) and a special study of the aerosol in New York City in the summer and winter. The SURE program is also making complementary measurements in essentially the same geographical region as MAP3S, and both networks have a common station at Rockport, 1N, for purposes of intercomparison between the two programs.

Fine particle samplers located in the MAP3S aerosol acidity network consist of automated Lundgren cascade impactors that collect four-hour samples of size-classified particles (see Table 6.1). The locations of the samplers and the dates they were deployed are shown in Table 6.2. The samples from Stage IV (nominal size 0.3 to 1.0 μm aerodynamic diameter) are analyzed quantitatively for ammonium, nitrate, and neutral sulfate ions, and qualitatively for acidic sulfate and other

Stage No.	Particle Aerodynamic Diameter, μm
I	10
II	10-3
III	3-1
IV	1-0.3
After Filter	< 0.3

TABLE 6.2. Network Locations and Dates of Operation

Site	Date Sampling Started
PSU, University Park, PA	February 16, 1977
UOV, Charlottesville, VA	May 10, 1977
ANL, Argonne, Il[*]	June 15 to July 13, 1977
R-1, Rockport, IN	July 28, 1977
BNL, Upton, NY	December 14, 1977
RLN, Raquette Lake, NY	October 19, 1978

[*]Temporary site.

constituents (see Section 5.1.2.2 for a description of the analyt
method).

Figure 6.1 shows the average monthly loading of the particles in
0.3 to 1.0 μm aerodynamic diameter size range at the various s
Although relatively complete information is available only from PSU
is evident that the fine particle aerosol loadings peak during the sum
and are lowest in spring and fall. The aerosol loadings at PSU and
appear to correlate well with each other, suggesting that this behavi
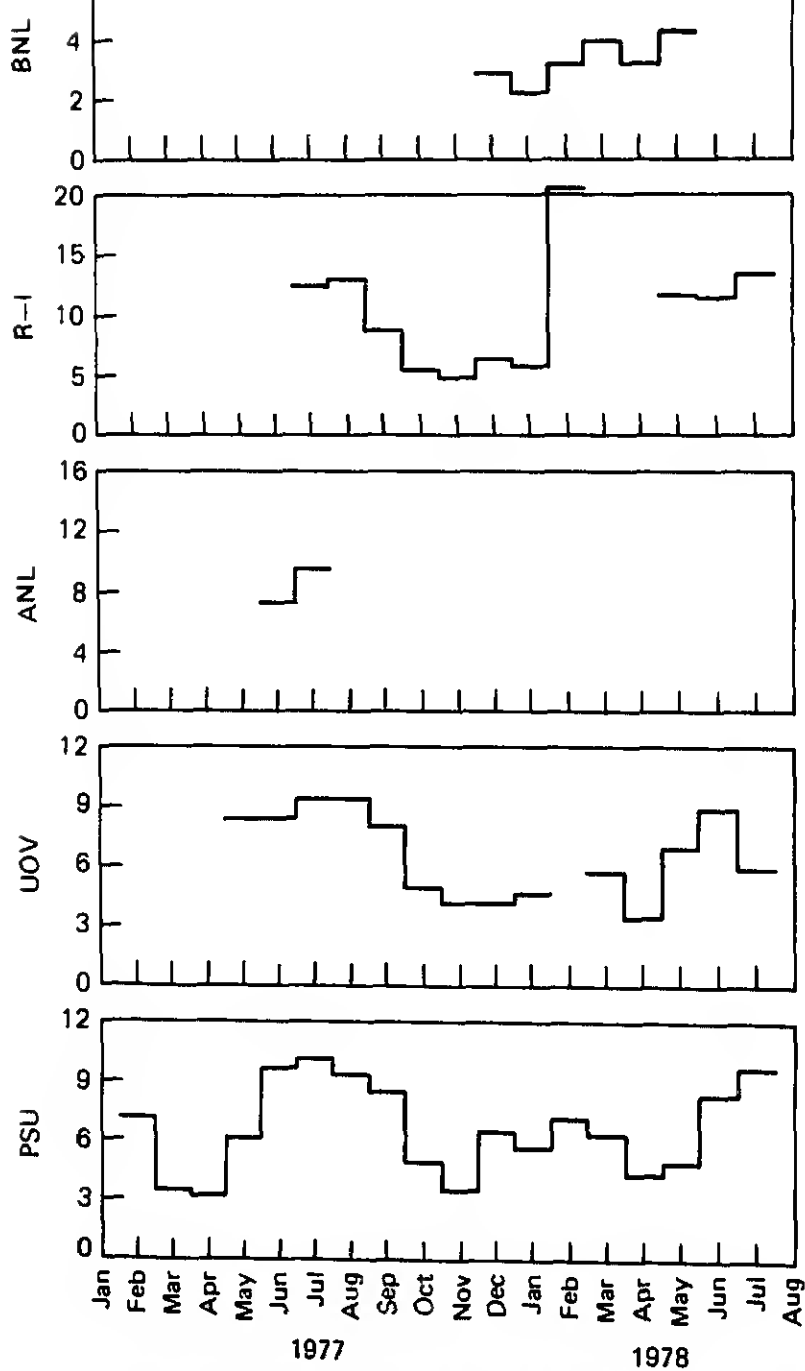
FIGURE 6.1 Average monthly aerosol loadings (0.3-1.0 μm radius

Figure 6.2 shows the diurnal behavior of fine particle loading, neutral sulfate, ammonium, and sulfate acidity at the various MAP3S sites. A distinct, and similar, diurnal pattern of aerosol loading is evident at PSU and UOV. The patterns at ANL and R-I, although similar to those at PSU and UOV, are not prominent. The aerosol loading at BNL also has a pronounced diurnal pattern but one that is out of phase with the diurnal variations at the other sites, leading the latter by about eight hours (all times are in local standard time). Diurnal variations are also observable in the other variables plotted in Fig. 6.2. The variation in acidity at BNL is again out of phase with that at PSU or UOV by 12 hours, but does not have as symmetrical a cycle as at the other two sites.

An important result obtained so far is that the ambient aerosol is essentially neutral at Rockport, IN, and ANL, but highly acidic at BNL. Aerosol at PSU, and Charlottesville, VA, is slightly lower in acidity than that at BNL, but is considerably more acidic than the aerosol at Rockport, IN, or ANL. (There is very little information from Racquett Lake, NY, since that sampler has only recently started operating.)

The observation that aerosol acidity is considerably greater in the eastern states than in the Midwest is in contrast to the fairly uniform acidity of the precipitation in much of the MAP3S region (see Sec. 6.4). It will be of interest to see if the fine particle aerosol loading and acidity can be correlated with the precipitation chemistry and atmospheric turbidity at these sites.

The results described above are based on the averaged values of the various quantities measured and/or calculated. However, due to the scatter in these data (in general, the standard deviation in any sub-set of the data is of the order of the value of the mean), these results must be interpreted with caution. Further, although the data base consists of more than 1300 observations, it is still very limited in that trends such as seasonal variations cannot readily be deduced. With continued sampling and analysis, however, this data base should become more representative and reliable.

As a means of deriving precipitation scavenging ratios for aerosols, weekly sampling of aerosols on 0.8 µm pore diameter Nucleopore filters was begun by ISWS in May 1977 at the Whiteface Mountain, NY and Charlottesville, VA MAP3S precipitation chemistry network sites. Samples have also been collected since June 1975, at Champaign, IL, where collection of MAP3S precipitation samples began in November, 1977. Sampling was suspended at all three sites in May 1978, however,

	Loading	Sulfate	Ammonium	Acidity
BNL				
R-I				
ANL				
UOV				
PSU				

Time of day
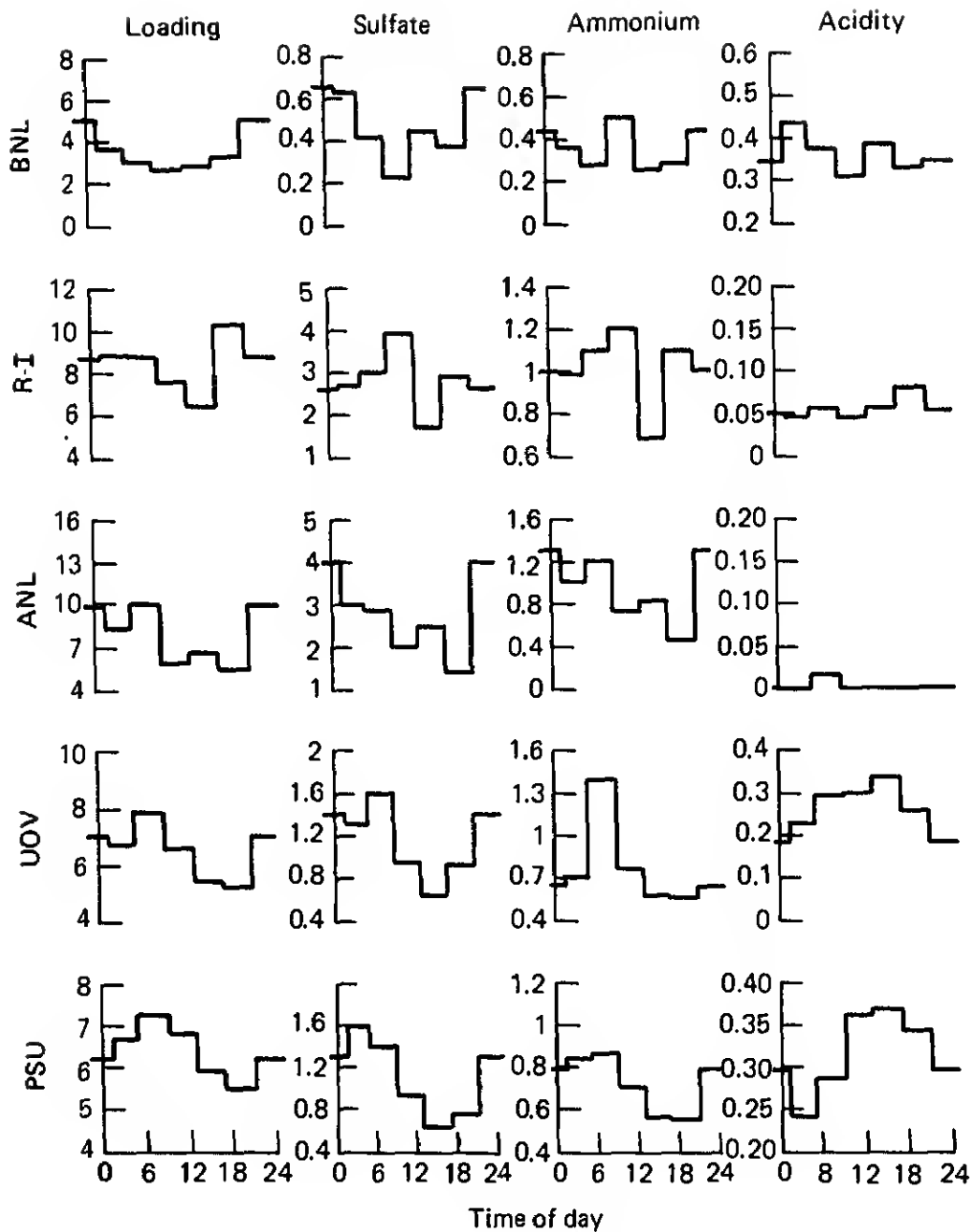
for ions or elements that occur in both aerosols and precipitation.

During the same period that detailed plans for MAP3S were being formulated in 1976, a group of participants from six organizations (NYU, Yale, EML, ISC, URI, BNL) with shared research interests in the nature and sources of urban aerosols met to develop a collaborative study of the New York metropolitan aerosol with the goal of a detailed characterization of the New York City aerosol in both summer and winter seasons.

The study was conducted during July and (principally) August 1976, and during February 1977, at a site in central Manhattan supplemented by limited measurements at an upwind site in High Point, NJ. Sampling at four sites - Manhattan; BNL; New Haven, CN; and High Point, NJ - were also conducted during three later periods (July-August 1977; January-February 1978; and July 1978) using a more limited set of chemical and meteorological instrumentation and improved analytical methodologies for sulfur- and nitrogen-containing constituents. A summary of sampling and analysis methodologies is given in Table 6.3.

The results of the New York Summer Aerosol Study (NYSAS) have been reported in summary form (Leaderer, 1978) and are to be published in early 1979 as a set of papers in <u>Annals of the New York Academy of Sciences</u>. Data from the winter and summer 1977 sampling periods are reaching final form and detailed comparisons of winter and summer aerosol composition in New York are, with one exception (Tanner et al., 1978), only now being formulated. Data from subsequent sampling periods are still incomplete, but some data on aerosol composition results are directly related to the MAP3S characterization task and provide some indications of sub-regional trends in aerosol sulfate and nitrate.

The existence of respirable aerosol sulfate in the ambient environment, predominantly in the chemical form of sulfuric acid mostly neutralized by ammonia, is now well documented (Tanner et al., 1977; Stevens et al., 1978). The average composition of fine particulate (≤ 3.5 μm) sulfate in summer, 1976, New York aerosols was approximately that of letovicite $[(NH_4)_3H(SO_4)_2]$. Based on the impactor data, about 85% of the aerosol sulfate was in the fine particle fraction. About 50% of this aerosol sulfate was deduced to be in the suboptical size regime (≤ 0.25 μm) from diffusion processor data. The $H^+/SO_4^=$ ratio in suboptical aerosols did not significantly differ from that in fine fraction aerosol. The coarse particle sulfate was not associated with H^+ or NH_4^+ and comprised about 15% of the sulfate mass.

Thus it was found that aerosol sulfate concentrations in summer were

TABLE 6.3. New York Aerosol Study Measurements

Measured Parameter	Sampling Method	Time Resolution hr	Sampling Period	Sampling Method or Sensor Principle
osol Sulfate	HiVol Filter	24 hr	S76,W77	Turbidimetry
	HiVol Filter	6 hr	W77,S77	Turbidimetry
	HiVol Filter	6 hr	W77-S78	MTB Colorimetry
	HiVol Filter	6 hr	W77	Ion Chromatography
	HiVol Filter	3 hr	S77,S78*	MTB Colorimetry
	Diffusion Sampler	12 hr	S76,W77	MTB or Turbidimetry
...O4	HiVol Filter	6 hr, 3 hr	S77-S78	Benzaldehyde Extraction
osol Nitrate	HiVol Filter	24 hr	S76,W77	Reduction-Colorimetry
	HiVol Filter	6 hr	W77-S78	Reduction-Colorimetry
	Diffusion Sampler	12 hr	S76,W77	Reduction-Colorimetry
ng Acid	HiVol Filter+	6 hr	S77-S78	Gran Titration
	Diffusion Sampler	12 hr	S76,W77	Gran Titration
monium	HiVol Filter	24 hr	S76	Indophenol Colorimetry
	HiVol Filter	6 hr	W77-S78	Indophenol Colorimetry
	Diffusion Sampler	12 hr	S76,W77	Indophenol Colorimetry
osol Mass	Continuous	1 hr	S76-S78	Nephelometer
	HiVol Filter	24 hr	S76,W77	Gravimetry
	HiVil Filter	6 hr	W77-S78	Gravimetry

TABLE 6.3. Continued.

Measured Parameter	Sampling Method	Time Resolution hr	Sampling Period	Sampling Method or Sensor Principle
Size Distribution	1-6 min Avg/hr	1 hr	S76, W77	EAA
	1-6 min Avg/hr	1 hr	S76, W77	Diffusion Battery-C
	1-6 min Avg/hr	1 hr	S76-S78	Optical Counter
Trace Metals	HiVol Filter	24 hr, 1 wk	S76, W77	Atomic Absorption
	Cyclone Sampler	24 hr, 1 wk	S76-S77	Atomic Absorption
	HiVol Filter	6 hr	W77-S78	Atomic Absorption
Halogen Compounds	HiVol Filter	1 wk	S76, W77	NAA
Light Scattering	Continuous	1 hr	S76, W77	Laser Backscatter
	Continuous	1 hr	S76, S78	Nephelometer**
Relative Humidity	Continuous	1 hr	S76-S78	Wet/Dry Bulb
Dew Point	Continuous	1 hr	S76-S78	
Temperature	Continuous	1 hr	S76-S78	
Wind Speed	Continuous	1 hr	S76-S78	
Wind Direction	Continuous	1 hr	S76-S78	

*BNL and NYU site only

+Quartz filters only; no valid New York data.

** Aerosol Mass/Nephelometer.

rather than being formed there.

The data from the winter, 1977, sampling period were substantively different than observed in the summer (Tanner et al., 1978). Sulfate concentrations were lower, fine fraction sulfate was more nearly neutralized by NH_4^+ ($H^+/SO_4^=$ < 0.10), and, based on diffusion sampler data, aerosol sulfate may have been in somewhat larger particles on the average than in the summer. Analysis of diurnal trends from 6-hr HiVol sampling indicates maximum sulfate concentrations during the morning (06-12 hour) period, but closest association of sulfate with ammonium was during the early morning (00-06 hour) period (r = 0.9).

Investigation of the spatial variability of sulfate concentrations in the New York subregion with inclusion of summer, 1977, and winter, 1978, data is still in progress. It does appear that sulfate concentrations were elevated in New York relative to an upwind rural site by from 3-6 $\mu g/m^3$ during the winter, 1977, sampling period, in contrast to summer, 1976, when elevated urban values were not observed.

Sulfate values in the subregion were remarkably constant during July-August, 1977, at the four sites, except where attenuated by local meteorological variations such as frontal interposition and precipitation. Nitrate concentrations were elevated at New Haven with nighttime maxima, and ammonium/sulfate ratios were higher (and $H^+/SO_4^=$ lower) at both New Haven and BNL sites as compared to the High Point, NJ site. Pronounced afternoon maxima in acid and sulfate concentrations were observed at the BNL site alone. The relevance of the interposition of the urban area between these sites during prevailing wind direction is not yet clear. Further statistical treatment of data is in progress.

Due to the regional nature of and the high temporal correlation between elevated sulfate values, lowered visibility, and high oxidant concentrations, assessment of urban air quality in the northeast U.S. requires a knowledge of the history of air masses reaching the urban area to deduce quantitatively the relative roles of local emissions and regional transport in affecting local concentrations of sulfur and nitrogen compounds. It is believed that this data base, when combined with SURE ground sampling data and MAP3S airborne characteristization measurements, will contribute to achieving the capability for relating emissions to regional pollutants, including aerosol sulfur and related species.

Information on the vertical and horizontal pollutant distribution is essential both to evaluate the nature and extent of the air quality problem and to gain an understanding of the transport and transformation of atmospheric pollution on a regional scale. The use of aircraft as atmospheric measurement platforms provides the most direct, and in some cases the only reasonable, means to gather the required data. Therefore, aircraft measurements have become an important component of the MAP3S program. The BNL atmospheric science aircraft was equipped and the PNL atmospheric science aircraft* was relocated primarily in response to the MAP3S program. A variety of experiments have been designed and conducted utilizing the unique capabilities of these aircraft. Figure 6.3 shows the two aircraft prior to a coordinated mission for MAP3S. Two additional aircraft operating for the EPRI-SURE program, sometimes operating in cooperation with the MAP3S aircraft as the result of joint meetings to plan measurement protocols, helped develop a data base during the SURE intensive periods. Together with data from the more than 50 surface measurement stations that were also operating, these data sets will provide a significant resource for further study and model evaluation.

The equipment installed in these four airplanes is designed to measure a variety of physical and chemical parameters. All of the aircraft have instruments for real time measurement of temperature, relative humidity and other meteorological parameters as well as concentrations of nitrogen oxides, sulfur compounds and ozone. Equipment to collect discrete samples of aerosol and sulfur dioxide are also included in these aircraft. In addition certain of these aircraft have instruments to measure solar radiation, aerosol size distribution and concentration, hydrocarbons and winds. These aircraft may also be equipped with special purpose apparatus to suit specific experimental purposes.

6.2.2 Preliminary Results

The capabilities of these aircraft to make atmospheric measurements in the horizontal and vertical dimensions strongly influenced the design of experiments for MAP3S. The additional possibility of cooperative studies with several of these aircraft added another dimension to field study concepts. Experiments that were considered impossible a few years ago have therefore been tried.

The first airborne MAP3S experiments were process-oriented studies of the scavenging of pollutants by precipitation conducted with the PNL aircraft in March of 1977 (see Section 10.1). Investigations of chemical

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*For some studies, two aircraft were made available by PNL.

FIGURE 6.3. The BNL Douglas DC-3 and BNL Britten-Norman Islander atmospheric science aircraft th...

The BNL aircraft became operational in time for the first MAP3S-SURE cooperative program in July 1977. The initial phase of this joint effort was a four aircraft intercalibration at Lewisburg, West Virginia. Although the pollutant concentrations were low during the flights, the real time instruments showed good agreement. The results of the filter intercomparisons however, led to the subsequent effort to add an additional, identical sampling instrument to all aircraft to permit intercomparison of results. In the first two weeks of August 1977, the MAP3S regional characterization and SURE-Intensive were scheduled to run concurrently. During this exercise the BNL aircraft attempted to characterize the regional distribution of pollutants within the well-mixed layer in the area defined by Upton, NY; Montague, MA; Scranton, PA; and Indian River, DE (the last three sites are SURE Class I station sites). The PNL aircraft conducted several regional characterization studies in the Michigan, Ohio and Indiana region including participation in an intensive effort to develop a pollutant cross-section along the Ohio River Valley (see Section 7.1). The EPRI-SURE aircraft examined the vertical distribution of pollutants in the vicinity of the SURE class one stations at Lewisburg, WV, and Philo, OH.

Initial analysis of the data from the August 1977 horizontal pollutant distribution studies shows that the sulfate to total sulfur ratio of the pollution over the northeast region varies markedly (from 0.2 to 0.6). Generally situations dominated by local sources may be expected to have low sulfate to total sulfur ratios whereas those arising from long range transport would be expected to exhibit high ratios. Sulfate and sulfur dioxide concentrations measured during two of the horizontal studies are shown in Figs. 6.4 and 6.5. The sulfate to total sulfur ratios suggest that a combination of local emissions and long-range transport contribute to the sulfur pollution in the northeast U. S. Further, the sulfur dioxide concentrations apparently have more spatial variability than those of sulfate, probably induced by distribution of local sources. Results from the continuous monitors indicate that the variations in sulfur concentrations are smoother than suggested by the integrated sample results. Detailed analyses of these measurements are presently in progress.

Another multi-aircraft study was carried out during SURE Intensive V in July 1978, based on an intent to further evaluate a particular weather type that occurred in in August 1977 and led to apparent long-range pollutant transport. in mid-July, a large high pressure area moved in and stagnated over the MAP3S-SURE region setting up episodic pollution
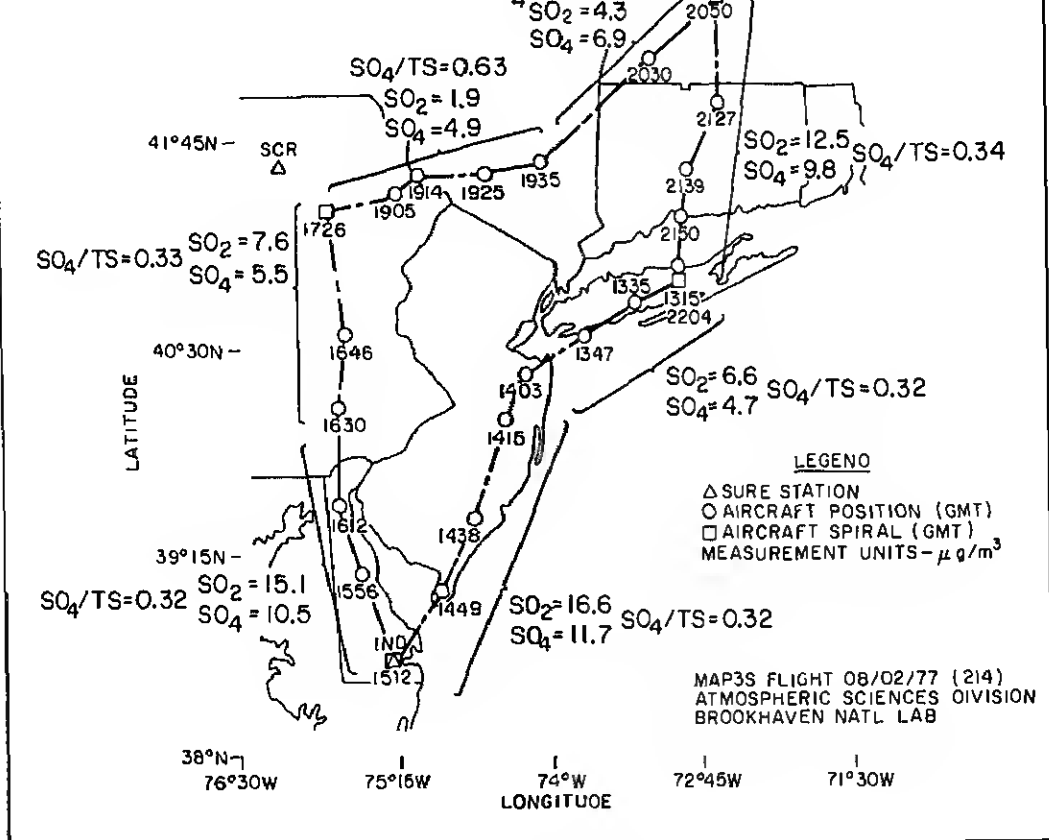
FIGURE 6.4 Results of regional characterization flight of August 2, 1977 showing SO_2, SO_4^- and SO_4^-/total sulfur on flight path encircling New York City-Philadelphia area.

worked out jointly by SURE and MAP3S researchers. Two aircraft were flown by PNL and one each by BNL, RTI, and MRI on the flight routes shown in Fig. 6.6. Extensive measurements of the pollutant concentration were made over the region, providing data on the build-up, the geographic extent and the horizontal and vertical distribution during the episode. Analysis of the data from this experiment is underway. Another such cooperative airborne study was planned for SURE Intensive VI in October 1978; however, a combination of poor meteorological conditions and aircraft operational problems caused cancellation of this study.
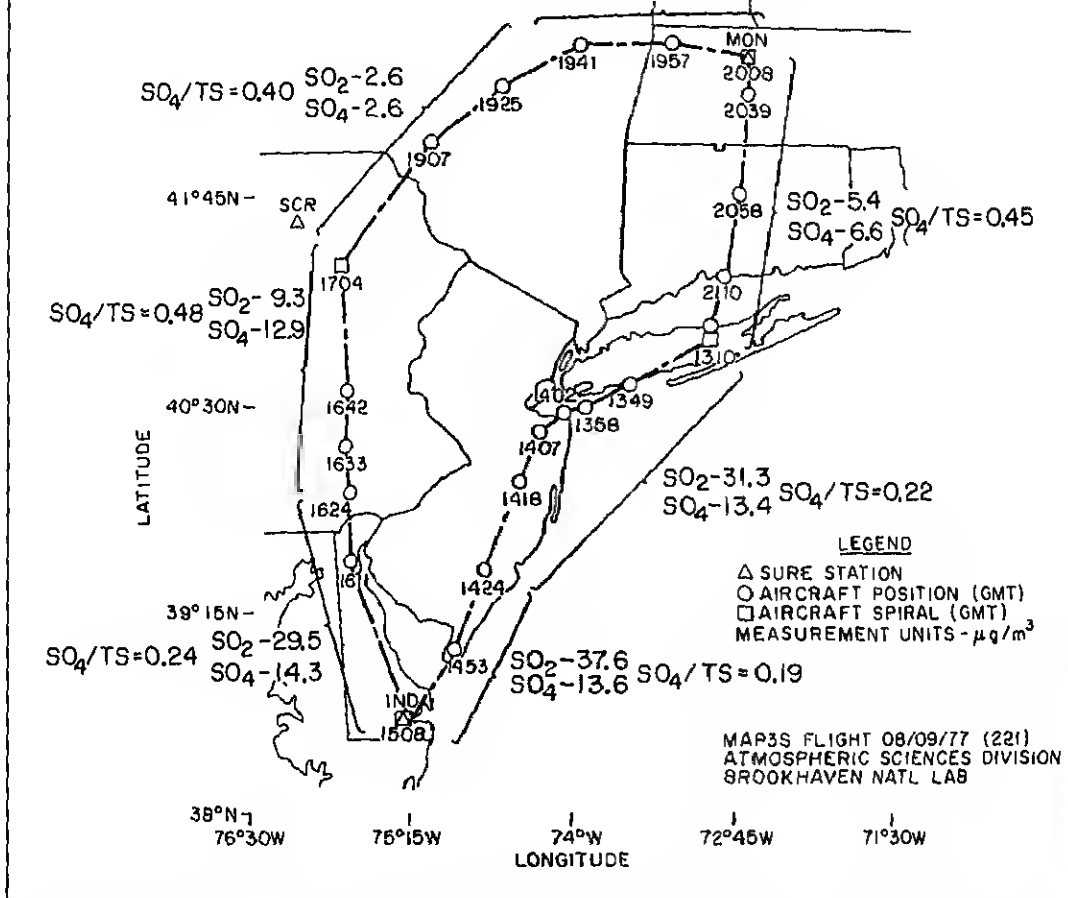
FIGURE 6.5 Same quantities as Fig. 6.4, except for August 9, 1977.
Note the north-south differences in SO_2 and $SO_{\overline{4}}$ that
result due to the presence of air masses with different
histories.

The SURE aircraft have now completed six intensive studies. These
experiments were conducted in the vicinity of SURE class one fixed
ground monitoring stations. The experiments consisted of vertical
distribution measurements from near ground level to 3 km in height. The
profile locations were generally directly over the ground station and at
points upwind and downwind from the ground station location. The
experiments were performed on alternate days during each twelve day
intensive period. During each day of operation flights were made near
sunrise and at midday to observe atmospheric structure changes brought
about by mixing.
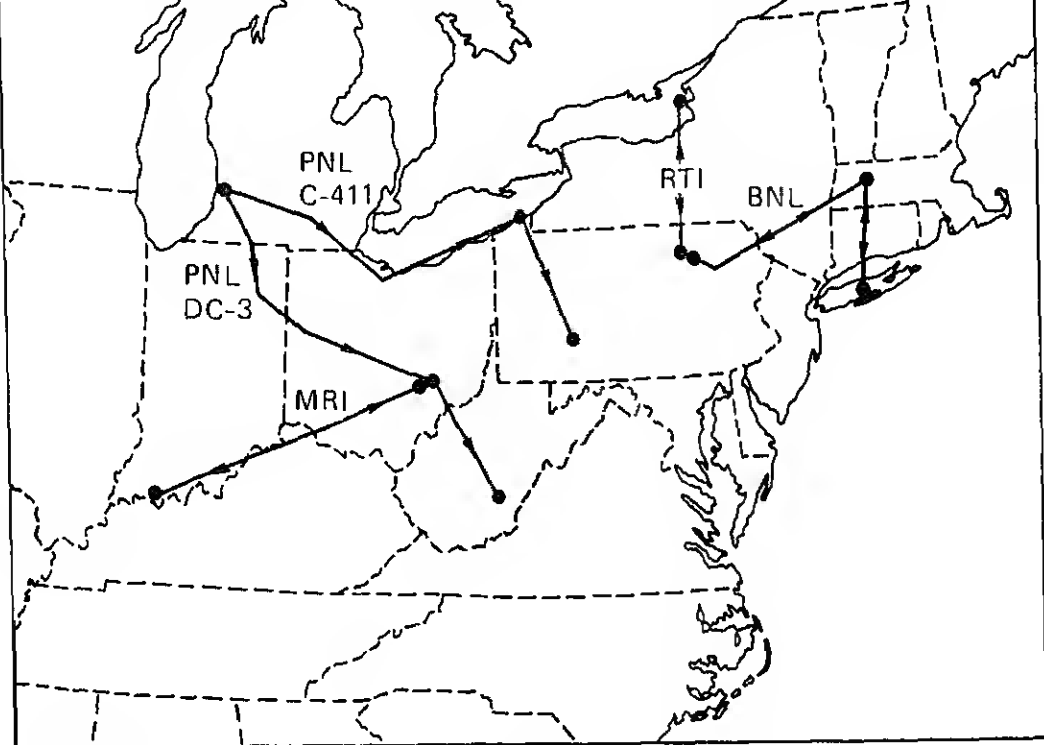
FIGURE 6.6 Flight plans of the three MAP3S and two SURE aircraft on July 19, 1978, as part of the intensive measurement of long-range pollutant "ducting" conditions. The PNL flight plans on July 20 were flown in the opposite direction.

The BNL airborne research group conducted a series of vertical pollutant profiles over central Long Island scheduled in coordination with SURE Intensive III in January 1978. Urban plume studies in the vicinity of the New York metropolitan area occupied the BNL Islander during SURE Intensive IV in April 1978. Results from these experiments are now being analyzed.

The extent of pollutant advection taking place above the mixed layer that may contribute to long-range transport and dilution of surface concentrations remains a major unanswered question. The vertical pollutant structure studies were aimed primarily at investigating this situation. Preliminary analysis of the experimental data indicates that significant quantities of material can be transported above the mixed layer under certain meteorological conditions. Material from the surface

generally quite high, indicating that the material had been
over regional scale distances (Michael et al., 1979).

6.2.3 Future Activities

The data collected by the MAP3S and SURE aircraft programs will be
of immense value to improving the understanding of atmospheric
pollution and the processes that affect its transport, transformation and
removal. Many of the experiments outlined above are continuing and
new experiments are planned that will generate a more complete data
base. The cooperation of the SURE program with the MAP3S,
particularly with respect to the airborne operations, has provided
significant benefits to both programs. The experimental design, the data
base, and the analysis of results have all been improved from this joint
effort.

During 1979, MAP3S will devote a substantial effort to detailed
analyses of the experiments carried out thus far. As the analyses
proceed, new approaches to characterizing regional air quality will be
developed based upon deficiencies in the data base. Only very limited
characterization studies will be conducted during this period, however, in
part due to the end of the extensive SURE surface measurement
program. These experiments are expected to primarily consist of a
continuation of measurement series started during the first two years of
the program.

The only cooperative study presently planned and related to regional
characterization is an intercalibration of the two MAP3S aircraft,
scheduled for the spring of 1979 at BNL. Intercalibration and cross
laboratory analysis will be carried out on the ground and during joint
flights for all jointly measured experimental parameters. With the end
of the SURE field program, MAP3S will formulate plans for future
characterization studies in concert with major EPA programs.

Rather than focus on regional characterization of air quality, the
aircraft program will focus more on field experiments. The Battelle
group are expected to continue their field experiments investigating
precipitation scavenging and transformation processes in the urban
plume. Studies involving measurement of vertical pollutant profiles, the
New York urban plume and sea breeze effects will be the focus of the
BNL aircraft group.

6.3 REGIONAL PRECIPITATION CHEMISTRY NETWORK

Several factors led to MAP3S taking a leading role in establishing a network to sample precipitation chemistry. Long-standing evidence from Europe and increasing evidence from the United States indicated that energy-related pollutants were causing important changes in precipitation chemistry, and that the ecological effects of such changes could become very important. Data in the northeastern United States, however, were too limited to permit establishment of definitive relationships between source emissions and deposition many hundreds of kilometers away. Further, despite growing interest among a number of university researchers, there was no focus for creation of a network. MAP3S provided a rationale, a thrust, and necessary funding to get such a network started. Data from the recently established long-term National Atmospheric Deposition Program (NADP) and of a nine station EPRI network will be interfaced with the MAP3S results during the next year.

The overall objectives of the MAP3S program dictated several a priori requirements for the precipitation chemistry network to be operated as an integral part of the project. It was clear that precipitation event sampling would be required to support episode modeling. In addition, wet and dry deposition had to be separated in collected samples to allow evaluation of the two pollutant budget components. Rapid chemical analysis and reporting of results would be required for timely use of the data. Finally, with the early emphasis on sulfur compounds, it was desirable that the sampling methods attempt to allow evaluation of the previously largely unknown contribution of sulfur dioxide scavenging.

To promote effective operation of such a regional network, cooperation among researchers from DOE, NOAA, PNL, and several independent research organizations was sought. These independent groups, particularly university groups, offered a wide range of research experience in addition to their capability to maintain sampling sites. Minor additions to and adjustment of the MAP3S network objectives were needed to achieve their participation, but by merging this broader range of interests and through governance of the network by a committee of network participants, greater benefits to the study of precipitation chemistry were achieved than might have followed from attempted fulfillment of the MAP3S objectives without such cooperation.

Initial deployment of the network was coordinated by the Air

the scientific findings for their own research purposes led to very careful (and necessary) operational practices. The responsibility of PNL during this period involved mainly collector design and construction. A study of existing automatic precipitation samplers at the NOAA-sponsored test facility at Cornell University indicate that the HASL sampler was the best of existing samplers (Galloway and Likens, 1976, 1978). For MAP3S, PNL modified the HASL approach so as to reduce the possibility for loss of volatile species. The design that was selected (similar to the one depicted in Fig. 5.5) was the primary topic of business at the first network participants' meeting in February 1976. This meeting set the cooperative tone for collective decision-making among NOAA, DOE, PNL and network site operators that has continued through the two years of network operation. As a result of this meeting, certain changes to the original collector design were called for, and basic procedural details for sampling were established. The first four network sites (see Table 6.4 and Fig. 6.7) were also chosen at about this time.

A second meeting was held at Pennsylvania State University in July 1976, where the completed PNL (Battelle) collector (at this time still minus the refrigeration unit) was displayed, and sampling, analysis, and reporting methods were decided upon. Because of concern about the largely untested nature of the PNL collector and the efficacy of in-field deionized water rinse of the collector's funnel, two special studies were set up to accompany the initial period of sampling. First, the Environmental Measurements Laboratory (EML) provided the proven HASL collectors for backup and comparison purposes. Secondly, one network site was outfitted with a second PNL collector whose funnel would be acid washed between events for comparison with the sampler using a deionized water rinse. Sample collection began during the fall of 1976 at the first four sites; and the first monthly printout of pollutant concentrations was issued in January 1977.

Meanwhile, development of a collected sample freezing mechanism for the PNL collector proceeded. Upon discovery (through laboratory experimentation) that freezing of the sample was of no advantage over cooling to refrigerator temperature for preservation of sulfite ion (at least), the effort was transferred to refrigerator development. It was also found that chemical fixing of sulfite ion would be required, in addition to the cooling.

With most sampling procedures firmly established, the main topic of the third meeting in February 1977 was selection of additional sites. A number of prospective site operators made presentations during this meeting. Among the sites considered were Upton (Brookhaven), NY; Champaign, IL; and Lewes, DE. These three sites were selected by

Site Name	Site Number	Participating Organization
Whiteface Mountain, NY	1	Atmospheric Sciences Research Center, State University of New York at Albany
Ithaca, NY	2	Section of Ecology and Systematics, Cornell University
Penn State, PA	3	Department of Meteorology, Pennsylvania State University
Charlottesville, VA	4	Department of Environmental Sciences, University of Virginia
Champaign, IL	5	Illinois State Water Survey
Upton, NY	6	Department of Energy and Environment, Brookhaven National Laboratory
Lewes, DE	7	College of Marine Studies, University of Delaware
Oxford, OH	8	Institute of Environmental Sciences, Miami University

The meeting at Whiteface Mountain, NY in September 1977, featured the start of cooperation among the major precipitation chemistry networks of North America. Representatives of the Canada Atmospheric Environment Service CANSAP network, the U.S. Department of Agriculture NC-141 network (since renamed the National Atmospheric Deposition Program) and the Electric Power Research Institute SURE network were present. The first concerted effort among these programs, through the auspices of MAP3S, was the establishment of a collector comparison study to be located at the Pennsylvania State University site. The three types of collectors used by these networks are being compared on an event sampling basis for a period sufficient to establish good statistical analyses of collector performance.* This meeting also saw the establishment of a laboratory quality control program for the

FIGURE 6.7 Location of collector sites participating in MAP3S precipitation chemistry network.

MAP3S network, which began operation early in 1978 under supervision of EML.

The fifth meeting of network participants at Ithaca, NY, in May 19 consisted mainly of more formal reports from the site operators and MAP3S modeling community, describing present and prospective uses the MAP3S precipitation chemistry data.

Date	Event
August 1975	Collector survey/initial NOAA coordination
February 1976	Prototype PNL collector developed/first network participants' meeting, Silver Spring, MD
April 1976	Site survey
July 1976	Second participants' meeting, State College, PA
August 1976	Installation of PNL collectors at first four sites
September 1976	Site 3 (Penn State) in operation
October 1976	Sites 1 (Whiteface) and 2 (Ithaca) in operation
December 1976	Site 4 (Virginia) in operation
January 1977	First monthly data report issued
February 1977	Third participants' meeting, Charlottesville, VA
March 1977	Analyses of all PNL funnel rinses end
August 1977	Analyses of all HASL event samples end/beginning of TCM-fixing for sulfite analysis
September 1977	Fourth participants' meeting, Whiteface Mountain, NY
October 1977	First periodic summary report issued
February 1978	Sites 6 (Brookhaven) and 7 (Lewes, DE) in operation
May 1978	Fifth participants' meeting, Ithaca, NY/nine collector comparison study begins at PSU
June 1978	Weekly sampling (with full chemical analysis) with HASL collectors begins
October 1978	Site 8 (Oxford, OH) in operation

sites. The table also contains laboratory milestones reflecting the evolution of network procedures and special studies. Table 6.6 is a summary of network sampling and laboratory performance for the 21 month period through June 1978. Because of the special studies, there have been somewhat more samples fully analyzed than the total of network events. The ratio of special to routine network samples that were analyzed was high at first (about 3) due to HASL collector samples and PNL rinse samples; this ratio dropped to about unity just before the beginning of the PSU collector comparison study. Since the latter study provides nine samples for each event, the ratio is now about two. For the 21-month period there were 525 network precipitation events with 1100 samples fully analyzed and over 11,500 individual species analyses.

6.4 PRECIPITATION CHEMISTRY IN THE EASTERN UNITED STATES

6.4.1 Introduction

MAP3S has devoted considerable effort to gathering and interpreting information on precipitation chemistry in the eastern United States. A major failing of many network operations that require routine collection of samples and/or data is that the operators of the individual sites are less than enthusiastic about the objectives of the program. This lack of motivation leads to incomplete data sets, poorly collected samples, etc. The site locations for the MAP3S Precipitation Chemistry Network were selected in part with this problem in mind. In addition to the criteria that the sites had to be removed from local sources of atmospheric constituents and had to cover the northeastern United States, a third criterion was that the site operators had to be scientifically interested in the project and have a proven ability to work in the area of precipitation chemistry.

The ability of the MAP3S program to achieve this last criterion is reflected in the following compilation of research reports that the individual site operators have produced through their interaction with the MAP3S. The following reports represent an integration and expansion of the MAP3S objectives into the specific areas of research of the individual site operators. The research presented in these reports (Table 6.7) fulfills the MAP3S objective of developing a comprehensive data base and augments this in both a supplementary and complementary fashion by providing analysis and interpretation of the precipitation chemistry data being gathered.

6.4.2 Precipitation and Cloud Water Composition

The Atmospheric Science Research Center (ASRC) of the State

Number of Months:	21	
Average per Month:		
Network Events	25	Events whose data were reported – same-day events at more than one site are counted more than once.
Events per Network Site	5	
Samples Received	47	Received and eventually fully analyzed.
Samples Analyzed per Event	1.9	
Chemical Species Analyzed	490	
Average number of species analyzed per sample	10.5	

Whiteface Mountain, N.Y. A current computer file of the data sent to participating stations is maintained at SUNYA, Albany. This permits study of ion ratios, seasonal trends, period average deposition, etc. One particular area of study is the yearly reproducibility of the precipitation chemistry (or lack thereof).

As part of the routine operation of the Whiteface Mountain facility, the standard meteorological and solar parameters are monitored along with particles, ozone and certain selected trace gases at either or both the lodge (600 m) level and the summit (1500 m) level sites. The New York State Department of Environmental Conservation (DEC) does weekly bulk precipitation monitoring at several locations throughout the state, one of which is Whiteface Mountain. Their data are also being entered into the ASRC data file, which will soon permit a more comprehensive comparison study between the MAP3S and DEC sets of data. The summit site on Whiteface Mountain has also served as the location for a cooperative EPRI/SURE station for measurement of sulfur

TABLE 6.7. Reports on Precipitation Chemistry in MAP3S

Section	Supplemental Research Area	Collector Site	Supervising Organization	Operator
4.2	Precipitation and Cloud Water Composition	Whiteface Mtn., NY	SUNYA	R. Falcon
4.3	Trends in Acid Precipitation in the Eastern U.S.	Ithaca, NY	Cornell	G. Likens T. Butler
4.4	Within Event Precipitation Sampling	Upton, NY	BNL	G. Raynor
4.5	Intercalibration of North American Precipitation Collectors	State College, PA	PSU	V. Bowers R. dePena
4.6	Marine and Biogenic Contributions to Sulfur in Precipitation	Lewes, DE	Univ. Delaware	T. Church
4.7	Sulfur Deposition in Eastern United States	Charlottesville, VA	Univ Virginia	J. Galloway G. Parker
4.8	Acid Precipitation in Central Illinois	Champaign, IL	ISWS	G. Stensla
4.9	Seasonal Trends in Precipitation Composition	*	PNL	M. Terry

*This report has been prepared as part of the operation of the central analytical facility.

addition, a special particle collector was run for several months at the request of ISWS to provide data on trace metal concentrations.

The ASRC Whiteface Mountain Field Center is in a unique location. The main headquarters are at about the 600 m elevation on Whiteface Mountain with another observatory on the summit at about 1500 m. This offers the possibility of measuring the pH of cloud water (as opposed to just rain water) on Whiteface Mountain since there are many hours during each month in which a cloud envelopes the upper elevations of the mountain. An all plastic cloud water collector was developed to measure the acidity of cloud water.

During the summers of 1976 through 1978, cloud water was collected at the summit of Whiteface. It was found to be quite acidic. In fact, there have been a number of times when the water was significantly more acid than rain falling from higher clouds. Measurement of the pH of rain at the summit and at the MAP3S site at 600 m has shown that the rain may initially be less acid than the lower cloud water. However, after falling through the lower cloud, the pH measured at the 600 m level indicates that the rain has been further contaminated.

The cloud water collector has a special block through which the water may pass. This allows a pH probe to be inserted and a nearly continuous reading and/or recording of the change in pH during a cloudy period to be taken. Whiteface Mountain may have four to seven times more hours of fog than rain, thus the acid cloud water may be more of a problem than acid rain in mountain areas where low clouds are frequent.

One of the two cloud water collectors has been made portable so that it can be placed a short way up into the base of a low cloud. This allows us to obtain some idea of the difference, if any, in acidity near the base of the cloud as compared to that at the level of the summit.

Some preliminary results are available from these studies. Figure 6.8 shows the pH of rain and cloud water at a number of sites during a rainfall event on July 25, 1977. Figure 6.9 shows the variation in pH of cloud and rain water at the summit of Whiteface Mountain. The summit was covered by cloud from before noon until thunderstorm rain began at about 2:30 p.m. Note that the pH increased when the rain began, emphasizing the importance of the potential role of fog in indicating ecological effects.

6.4.3 Trends in Acid Precipitation in the Eastern U. S.
The historical record of changes in the acidity of precipitation in North America is difficult to discern due to the lack of a continuous
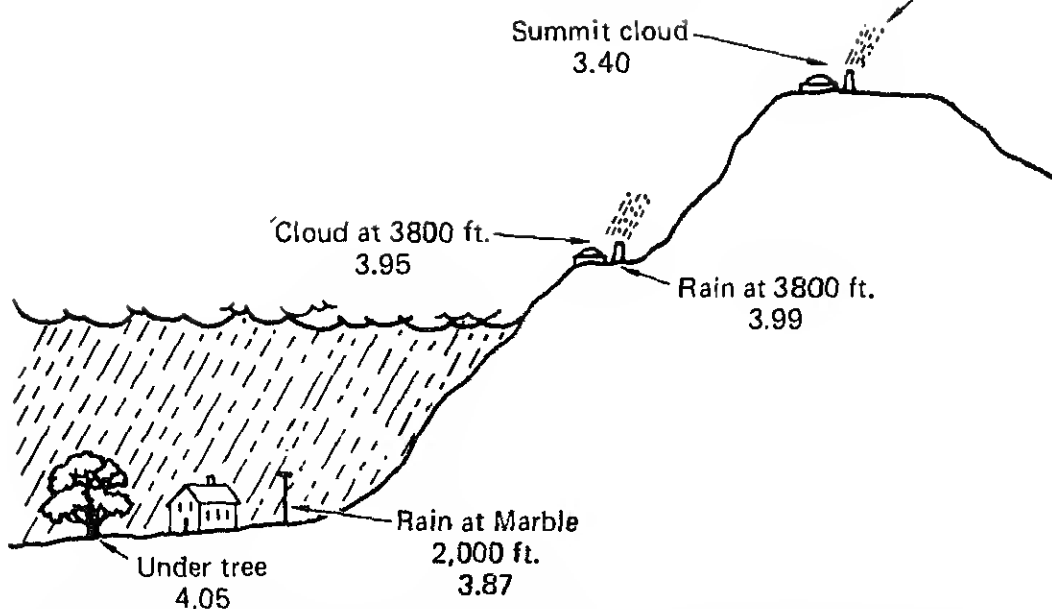
FIGURE 6.8 Simultaneous measurement of cloud and rain water pH at Whiteface Mountain, Wilmington, NY on the afternoon of July 25, 1977.

6.4.7.) Prior to about 1930, relatively large amounts of bicarbonate were found in samples of rain and snow in Virginia, Tennessee and New York State. Although no pH determinations were made, the presence of bicarbonate in these samples indicates that they cannot have had a pH value less than 5.6. The earliest known pH measurement of precipitation in the U.S. was made during a single rainstorm in 1939 in Brooklin, Maine by H. G. Houghton of MIT. A value of 5.9 was obtained.

If accurate chemical data are available, and if the hydrogen ion concentration is greater than about 3 μeq/liter, then reliable pH values can be calculated from a detailed chemical analysis of dilute aquatic solutions. Such chemical data were collected for precipitation with wet-only collectors at 24 sites in the eastern United States in 1955-56 by C. Junge, but no pH measurements were made. The chemical data, however, have been used to calculate the pH distribution (Cogbill and Likens, 1974). Although the density of sampling points is low, the general pattern is quite clear. A large area of the northeastern United States was subjected to acid precipitation by the mid-1950's. Unfortunately, this network of sampling stations was not continued.
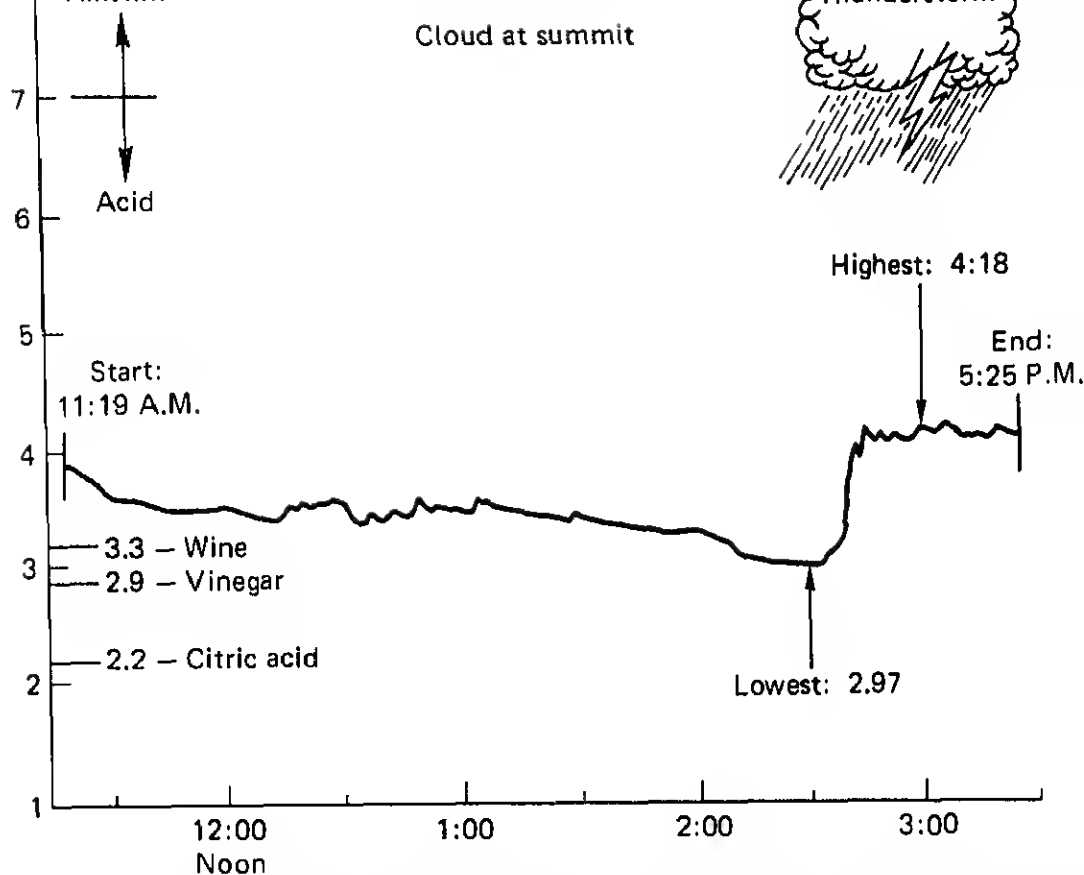
FIGURE 6.9 Continuous record of pH at summit of Whiteface Mountain on afternoon of July 25, 1977. Summit was covered by cloud from before noon until thunderstorm began at about 2:30 p.m.

During 1964 through 1966, the National Center for Atmospheric Research in Boulder, Colorado operated a sampling network for precipitation chemistry throughout the coterminous United States. Some 30 stations, 17 east of the Mississippi River, collected monthly precipitation samples with automatic, wet-only samplers. The vast majority of monthly pH values for stations west of the Mississippi River were consistently greater than 5.6, with modal values in the high 6's; only one monthly value (a Louisiana station) was recorded to be less than pH 5.0. In contrast, monthly values east of the Mississippi River were much

the paucity of data, the general pattern was quite obvious; areas of acid precipitation were widespread in the eastern U. S. with the most acidic rain and snow falling on New England, New York and Pennsylvania.

Even today there is no high-density, synoptic coverage of precipitation chemistry in North America, and the lack of historical data on precipitation composition limits our ability to determine man's effects on the chemical composition of the atmosphere. Currently, programs in Canada and the United States have begun to measure the composition of atmospheric deposition on a long-term basis. In Canada, the Canadian Network for Sampling Precipitation (CANSAP) was begun in 1976. In the United States, weekly sample collections were begun in July 1978 as part of the National Atmospheric Deposition Program (NADP), initiated by the State Agricultural Experiment Stations of USDA. This program will expand greatly the limited, but important, coverage of the MAP3S synoptic network.

In an effort to obtain synoptic data on the current pH of precipitation in the eastern U. S., all of the known individual workers, groups, state and federal agencies that were studying precipitation chemistry were contacted and asked to share their data on the pH of precipitation. The response was generous and enlightening. The density of points in the eastern U. S. is still low (46 stations east of the Mississippi River), but is much greater than it was in 1955-56 or 1965-66. These data show that there has been a southward and westward extension of the area subjected to acid precipitation, with a possible intensification of acidity in the northeastern and southeastern regions since the mid-1950's.

The quality and quantity of data available in 1975-76 are highly variable, and, as is the case with all of these efforts, only the general pattern may be discerned. Undoubtedly there is much local variation, or "fine structure", particularly close to power plants or urban centers, but data are not yet available to evaluate this detailed pattern on an annual basis. Nevertheless, the general patterns of spatial distribution of acid precipitation are reasonably consistent and clear.

It is worth noting that the southeastern U. S. has undergone the most rapid increase in precipitation acidity in the last two decades (the trends are more apparent in this area as opposed to the northeastern U. S. because a smaller amount of acid is required to produce an obvious change in precipitation acidity). Over the same time the southeast has had an increase in urban and industrial activity that would provide a regional source of anthropogenic emissions leading to the increased acidity. Recent studies (Husar et al., 1979) have shown that this

6.4.4 Within-Event Precipitation Sampling

Since June 1976 (before MAP3S sampling began at BNL), hourly precipitation samples have been collected at BNL for chemical analyses of their constituents using an automatic, sequential, precipitation sampler designed and built for this study (Raynor and McNeil, 1978, 1979). The study was designed to investigate changes in precipitation chemistry within precipitation events and to relate these changes to pertinent meteorological and other variables. This cannot be done with event samples (such as MAP3S collects) because of the changes in both meteorological conditions and chemical composition that typically occur within events. Longer term aims are to relate the contaminants to sources or source regions and to determine the mechanisms by which the materials become incorporated into the precipitation. It is believed that materials are removed by both in-cloud and below-cloud processes in the early stages of an event but that material in the later stages represents largely in-cloud scavenging. Thus, a study of the changes with time should give a measure of the relative importance of the two processes for each material of interest. Event averages are also calculated from the hourly measurements so that the BNL data can be compared with data taken elsewhere.

Samples are removed from the sampler as soon as possible after precipitation ends. Conductivity and pH are measured as soon as the samples arrive at the analytical laboratory. Concentrations of sulfate, nitrate, ammonium, sodium and chloride ions are normally measured within a few days and the samples are kept refrigerated in the meantime. Concentration data are measured in ppm and later converted to microequivalents per liter.

Meteorological data recorded with each hourly sample include precipitation amount and type, cloud type, synoptic situation causing the precipitation, wind direction and speed at a height of 108 m, and air temperature. Other input data include the date, the sample number within the data, time of beginning and end of each sample, duration the cover was open and event number within the month.

A statistical analysis of the first year of data has been performed (Raynor and Hayes, 1978). All hours were classified by meteorological or time parameters and the mean, standard deviation, and other statistical quantities calculated for each constituent separately within each class. Ratios of selected ionic species were also computed and analyzed in the same way, as were values of excess conductivity and excess sulfate. A similar but somewhat more extensive analysis of data from the first two years is now in progress.

is lowest during the summer, during thunderstorm precipitation and during cold front and squall line rain. These variables, of course, are not unrelated. Also, pH was lowest with westerly winds when contaminants of probably anthropogenic origin were highest, as might be expected from the coastal location of BNL. Concentrations of nitrate and sulfate (Fig. 6.10) were high when pH was low. Average concentrations of chloride and sodium were higher with strong winds from the ocean; however, chloride was present in nearly double the chloride/sodium ratio in sea water during all wind directions, thus suggesting other important sources of chloride.

Determination of possible source regions requires accurate trajectory analysis not only of the storm or frontal system as a whole but also of the air parcels above the station during each precipitation sample. This aspect of the study is not yet initiated but trajectories for a two-month period have been obtained and will be used in a pilot study to determine if consistent relationships between trajectory and degree of contamination can be ascertained.

A correlation and regression analysis was also performed to determine the relationships among the chemical constituents without regard to meteorology. A high positive correlation was found among concentrations of hydrogen ion, sulfate, nitrate and ammonium suggesting a similar origin or pathway for a substantial fraction of these materials. Sodium and chloride were highly correlated with each other, despite the excess chloride, but showed little or no correlation with other species.

A detailed investigation of hour-to-hour changes within precipitation events is just beginning but various patterns are apparent from the data and a few cases have been studied (Raynor, 1977). In one group of cases, an early decrease in concentrations occurs followed by a more or less steady state as shown in Fig. 6.11. In another group, rainfall amounts are too light or concentrations are initially too low for significant changes to be expected. However, many cases with average or greater concentrations and adequate rainfall amounts show no consistent trend with time. This may suggest that most of the material in the water originated at cloud level and little was washed out of the air below cloud level. However, the reasons for these varying patterns are not yet fully understood and need to be investigated further.

6.4.5 Intercalibration of North American Precipitation Collectors

In an effort to extend early comparison studies of the PNL and HASL collectors with respect to their measurement of sulfite (see Chapter 5.3),
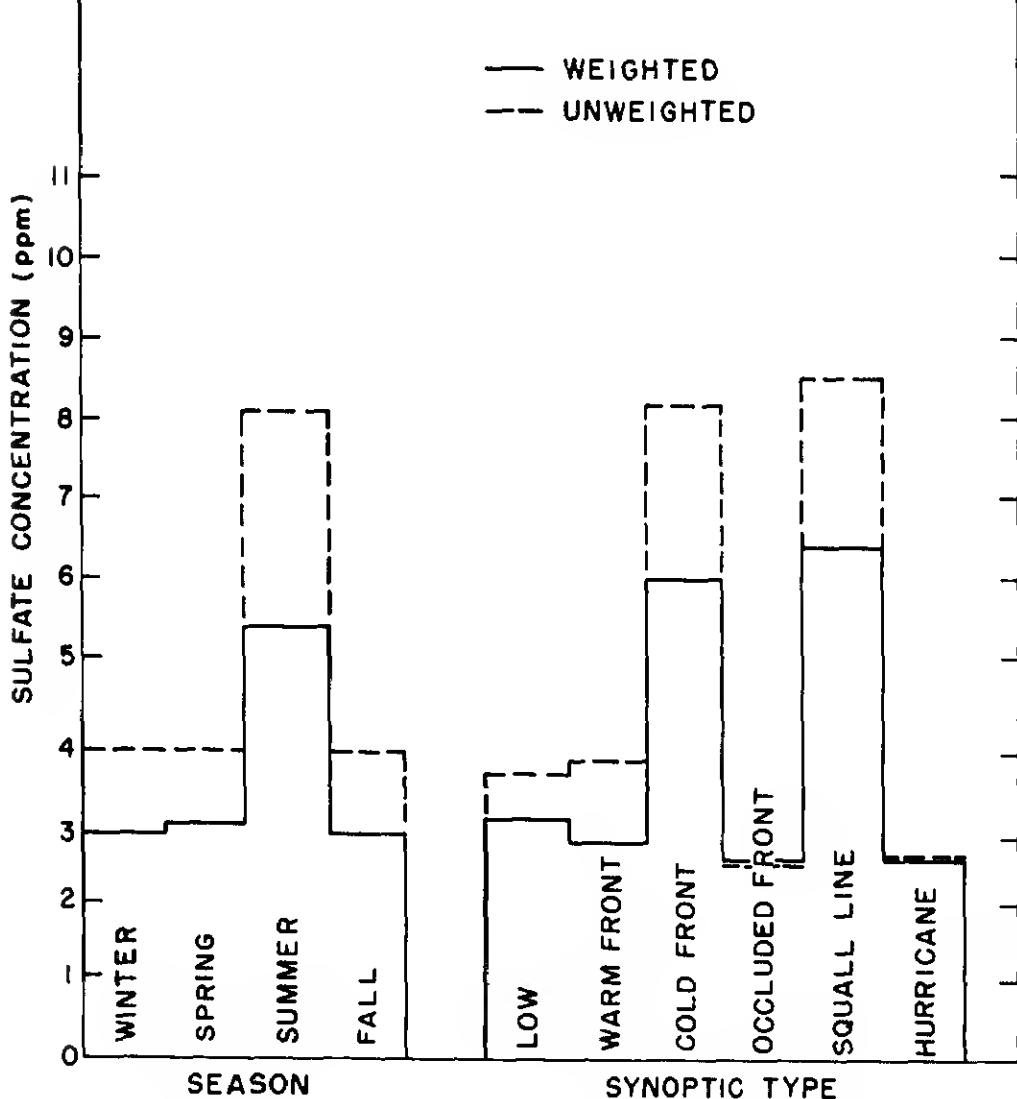
FIGURE 6.10 Variation of weighted and unweighted sulfate concentrations by season and synoptic type. Weighted means are weighted by precipitation amount.

also agreed to provide three of their collectors to increase the scope of the intercomparison. Together, the three types of samplers to be used in the study (the PNL sampler used by MAP3S; the commercial version of the HASL sampler used by NADP, EPRI, and others; and the CANSAP
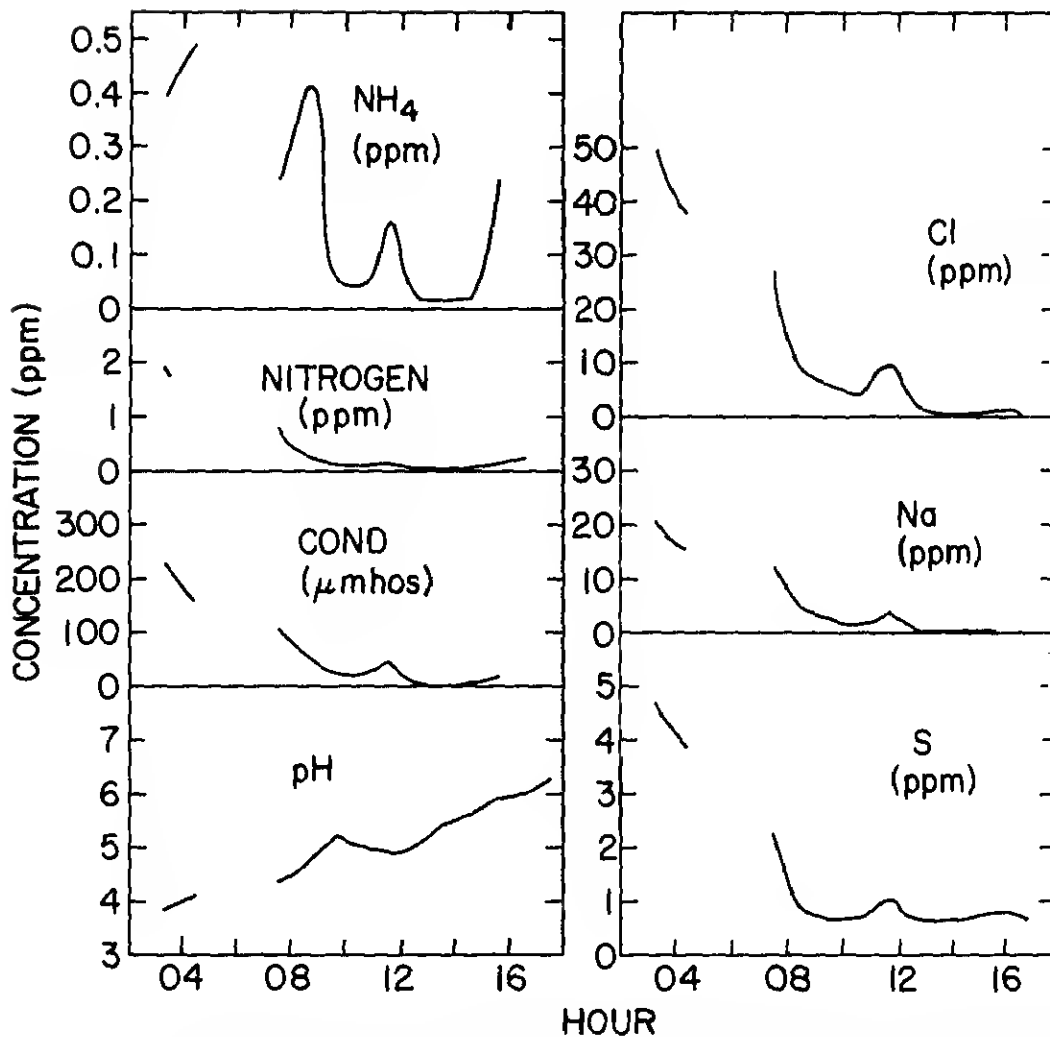
FIGURE 6.11 Variation in pH, conductivity and chemical constituent
with time during a rain of December 7, 1978. The gap
represent periods when rain was too light for an adequat
sample.

In late 1977, efforts were begun to select a site for th
intercomparison and to arrange for the samplers. The Pennsylvania Stat
University MAP3S site was selected because of its central location, it
staff resources, and the availability of other air quality measurements

for precipitation collection efficiency, a tipping bucket rain gauge was also installed at the site.

A total of 38 precipitation events have been sampled between the start of the operation and December 30, 1978. These events have included thirty-two rainfall(R), two snow(S), and four mixed(M) events. For fifty percent of the events, the maximum precipitation was 5 mm, and for half of these the precipitation was below 1 mm. For all the events the maximum precipitation observed was 28.7 mm.

Results of the chemical analysis of the first five events are given in Tables 6.8 to 6.10 (more recent events are still be analyzed). The relative concentration for the different chemical components using the data of the PNL collector as a standard, can be seen in Table 6.11. Until more sample results are available, the variability is such that it is not possible to draw any firm conclusions.

For the remaining 33 events the (H_3O^+), $(SO_3^=)$ and electrical conductivity L are reported in Table 6.12. These measurements have been made at PSU right after the sample were collected. Only samples with no visible contamination were analyzed, the others were discarded. In some instances the amount of sample was not sufficient for analysis.

The data on the amount of precipitation collected for each of the collectors and the rain gauge are given in Table 6.13. For each type of collector the mean value and the observed dispersion are given. As an index for dispersion the ratio

$$\text{range/mean} = \Delta/\overline{m}$$

is used.

A preliminary analysis shows that in the average the three types of collectors collect more precipitation than the rain gauge, especially when the precipitation event is above 5 mm. For precipitation events smaller than that value the correspondence with the rain gauge is closer, but the NC141 still collects more rain than the standard instrument.

With only five months of operation of collectors as part of the intercomparison study, it is apparent that a longer record will be required in order to have a sufficient number of cases on which to base conclusions. Clearly, there are now too few snow and mixed precipitation events to draw even preliminary conclusions.

| 8/1 | 77.6 | | 31.3 | 2.3 | 24.7 | 11.3 | | 0.68 |
| 8/4 | 121.2 | 0.23 | 54.3 | 4.7 | 28.8 | 17.0 | 1.6 | 3.3 |

TABLE 6.9. Collector CANSAP(C). All concentrations in (μ mol/liter).

Date	(H_3O^+)	$(SO_3^=)$	$(SO_4^=)$	(Cl^-)	(NO_3^-)	(NH_4^+)	(Na^+)	(Ca^{++})
7/24	82.2	0.28	46.5	5.5	26.5	12.9	2.9	9.3
7/28	202.6	0.37	88.0	6.9	51.0	24.0	1.0	7.6
7/30	179.8	0.42	115.0	16.7	89.7	46.3	1.9	33.0
8/1	77.0		35.0	3.3	26.7	15.0		1.1
8/4	124.0	0.21	52.7	4.3	29.0	18.3	1.5	3.9

TABLE 6.10. Collector NC141(N). All concentrations in (μ mol/liter).

Date	(H_3O^+)	$(SO_3^=)$	$(SO_4^=)$	(Cl^-)	(NO_3^-)	(NH_4^+)	(Na^+)	(Ca^{++})
7/24	95.5	0.27	44.0	5.1	24.3	16.5	2.4	8.9
7/28	202.6	0.36	82.7	6.2	50.0	21.0	1.3	5.0
7/30	158.5	0.38	84.0	15.0	73.0	32.5	3.6	24.5
8/1	78.8		36.0	3.2	28.7	10.7		0.80
8/11	123.0	0.17	51.0	3.9	26.0	20.0	1.9	3.3

TABLE 6.11. Relative mean concentration of different componen
using the P collector as a reference.

	(H_3O^+)	$(SO_3^=)$	$(SO_4^=)$	(Cl^-)	(NO_3^-)	(NH_4^+)	(Na^+)	(Ca^{++})
C/P	1.13	0.91	1.31	1.29	1.26	1.08	1.66	1.77
N/P	1.12	0.74	1.16	1.19	1.17	1.18	2.33	1.36

TABLE 6.12 Concentration of (H_3O^+), $(SO_3^=)$ and electrical conductivity L for the samples in the collectors P, C and N.

Date	(H_3O^+)(μmol/liter)			$(SO_3^=)$(μmol/liter)			L (μmohs/cm)		
	P	C	N	P	C	N	P	C	N
8/8	43	46	48	0.28	0.38	0.40	24.4	26.3	25.9
8/10	91	117	103	4.1	0.58	0.65	44.3		54.5
8/15	245	348	251	0.34	0.40	0.71	131	137	140
8/29	209	233	214	0.17	0.20	0.18	113	123	115
9/1	81	86	82	0.57	0.48	0.61	47.6	52.7	48.7
9/4	45	52	50	0.23	0.25	0.25	249	31.0	28.2
9/8	Insufficient amount of sample								
9/11	194		194	0.45	0.59	0.46			
9/13	157	157	154	0.30	0.29	0.24	85.7	87.4	83.0
9/15	421	444	476	0.21	0.23	0.24	24.7	25.8	26.7
9/19	127	125	123	0.30	0.37	0.27	72.6	72.7	70.3
9/25	296	617	337	0.84	1.00	0.95			195.0
9/28	324	372	316	0.92	1.0	0.83			
10/5	108	124	105	2.4	1.6	1.60	64.2	71.4	64.3
10/6	102	195	126	1.5	1.1	0.92			
10/9			79	0.56		0.92			
10/12	120	102	115	0.70	0.70	0.92			
10/14	85	91	93	2.2	1.90	2.2	48.7	52.1	49.2
10/17	137	129	126	4.0	3.0	3.3	74.2	80.0	74.6
10/19	331		603	0.73	3.4	0.73			
10/24	126	129	158	0.51	1.1	0.58			76.0
10/27	55	62	59	1.20	1.20	1.20	29.6	35.8	30.8
11/8	253	272	255	1.5	0.45	0.57	144	160	150
11/14	263	501	327	1.3	2.2	1.40	150	324	206
11/15	245	407	302	1.30	2.7	0.48			175
11/20	56	67	55	0.96	3.2	0.42	30.7	38.5	31.2
11/24	236	240	234	4.7	2.7	3.0	128	134	125
11/29	58	82	59	2.5	1.3	1.6	32.4	44.4	32.3
11/30	33	62	48	0.38	0.51	0.19			27.1
12/5	43	50	41	8.5	13.0	6.7	26.4	33.5	25.3
12/10	33	34	32	5.3	2.7	3.9	20.4	21.5	20.3
12/17	104	100	124	3.8	4.1	3.5			68.1
12/22	49	49	40	6.4	7.3	9.2	28.4	29.0	24.4

Precipitation	mm	mm	Δ/m	mm	Δ/m	mm	Δ/m
R	7.4	6.7	0.03	7.0	0.03	7.6	0.14
R	13.0	14.2	0.01	14.6	0.03	15.4	0.01
R	2.3	2.3	0.04	1.9	0.26	2.5	0.16
R	21.3	25.8	0.02	26.4	0.02	27.8	0.03
R	20.3	20.9	0.04	21.4	0.03	22.9	0.06
R	23.1	24.4	0.01	24.3	0.05	26.5	0.05
R	2.5	2.4	0.04	2.4	0.29	2.8	0.11
R	4.6	4.3	0.02	3.1	0.55	4.7	0.09
R	10.9	10.4	0.25	10.8	0.06	12.1	0.13
R	18.8	18.3	0.02	18.7	0.03	19.8	0.03
R	4.1	4.3	0.0	3.7	0.08	4.9	0.02
R		0.07	0.43	0.16	0.44	0.17	0.18
R	0.5	0.6	0.33	0.4	0.50	0.7	0.0
R	3.6	4.1	0.05	4.1	0.07	4.7	0.04
R	17.0	19.7	0.03	19.9	0.04	21.1	0.03
R	28.7	25.6	0.39	28.5	0.03	30.9	0.04
R	1.8	1.4	0.21	0.6	0.33	1.6	0.25
R	0.3	0.3	0.33	0.3	0.43	0.4	0.25
R	7.9	9.4	0.06	9.0	0.09	10.2	0.09
R	0.3	0.2	0.50	0.2	0.0	0.3	0.0
R	0.3	0.14	1.29	0.05	0.80	0.3	0.33
R	0.8	0.7	0.29	1.00	0.20	1.0	0.0
R	18.8	18.8	0.02	19.5	0.04	20.2	0.01
R	6.9	7.8	0.05	8.0	0.03	8.5	0.02
R	0.3	0.4	0.25	0.14	1.93	0.5	0.20
R	0.5	0.4	0.25	0.30	0.00	0.7	0.14
R	10.0	11.1	0.03	11.1	0.05	12.1	0.09
R	3.6	3.9	0.03	4.1	0.07	4.4	0.05
R	0.8	0.7	0.16	1.2	0.17	1.1	0.36
R	0.8	0.9	0.11	0.6	0.33	0.9	0.11
R	14.2	15.4	0.01	15.3	0.04	16.8	0.02
M	7.4	8.3	0.13	8.6	0.03	9.3	0.05
S	7.9	8.6	0.13	8.0	0.11	8.8	0.01
S	1.3	1.2	0.17	1.1	0.45	1.6	0.06
R	14.2	15.1	0.08	15.7	0.05	16.7	0.02
M	24.1	26.1	0.09	27.1	0.01	28.9	0.04
M	2.0	1.7	0.06	1.7	0.0	2.2	0.18
M	10.7	12.5	0.04	12.4	0.02	13.8	0.01

6.4.6 Marine and Biogenic Contributions to the Chemistry of Precipitation

6.4.6.1 Introduction

With the cooperation of the U.S. Navy, the seventh (of the eight) MAP3S precipitation stations was established on the Atlantic coast at the southern terminus of Delaware Bay at Lewes, Delaware. This location was selected for several reasons. First, previous measurements showed that the acid rain belt in the northeast reaches a maximum in the central Atlantic coastal region as it exits out over the ocean (e.g., Likens, 1976). Second, it was uncertain as to whether local effects of basic sea salt aerosol would contribute to neutralizing such acid rains. Thirdly, the area is characterized by extensive salt marshes that may contribute significant biogenic sulfur in the form of reduced gaseous sulfides emanating from the marsh surface. Some precipitation chemistry data are available for the Lewes area from 1977, but regular sampling did not begin until the late spring of 1978. The results offer the potential for evaluating the effect of the marine environment on precipitation chemistry.

6.4.6.2 Experimental Results

Based on the available data, a preliminary interpretation of the results has been performed.

pH

The complete record of pH at Lewes sites is shown in Fig. 6.12. The symbols represent all events collected and the horizontal bars the length of integrated automatic collection. There is a noticeable continuity in values in switching to the PNL collector and its relocation from near Lewes to the more remote Cape Henlopen site. The general pH trend, as for other MAP3S sites, is a decline and minimum in mid-summer months. Generally, rains at Lewes are distinctly acidic with values and trends matching those of other MAP3S sites.

Sea Salt Inputs

To assess the contribution of sea salt major ions (sodium, potassium, magnesium, calcium, chloride, and sulfate), plots were constructed of Mg^{++} and Na^+ versus Cl^- (Fig. 6.13), and $SO_4^=$ versus Cl^- and Mg^{++} (Fig. 6.14). The solid lines represent the stoichoimetry of sea salt. It is apparent that the bulk of sodium, chloride, and magnesium are from sea salt, probably of local origin. However, there is abundant excess sulfate and far more than could be contributed by sea salt.
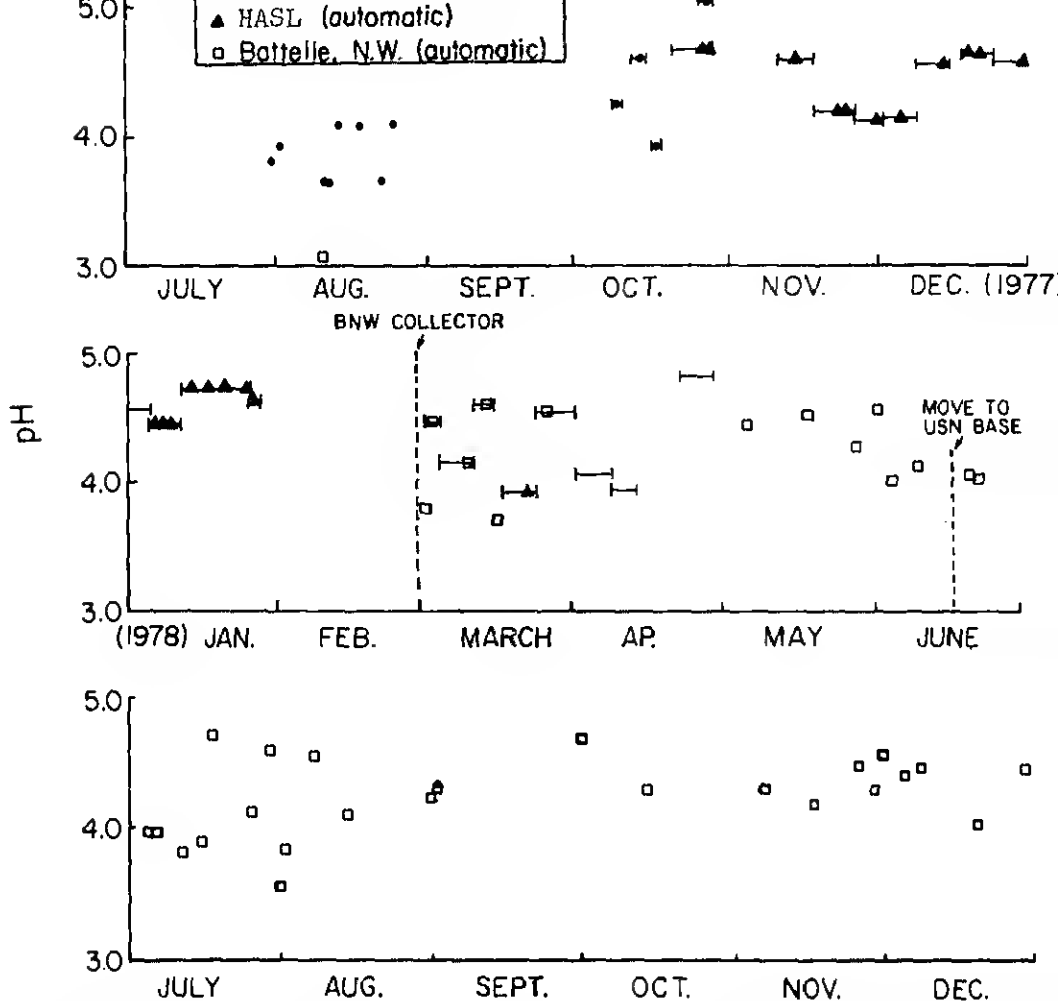
FIGURE 6.12 The monthly record of pH in rain water at Lewes, DE, including all sites monitored through 1978. Symbols represent all events and the horizontal bars are the length of integrated automatic collection.

Sulfate and Nitrate Acid Contributions

The cause of acidity in rain in the northeast U. S. is sulfuric and nitric acid, apparently from remotely transported and integrated products of fossil fuel combustion (Galloway, 1978). The rain data for Lewes were processed to calculate the mean monthly weighted precipitation contributions of sulfate, nitrate, protons and their ratios.
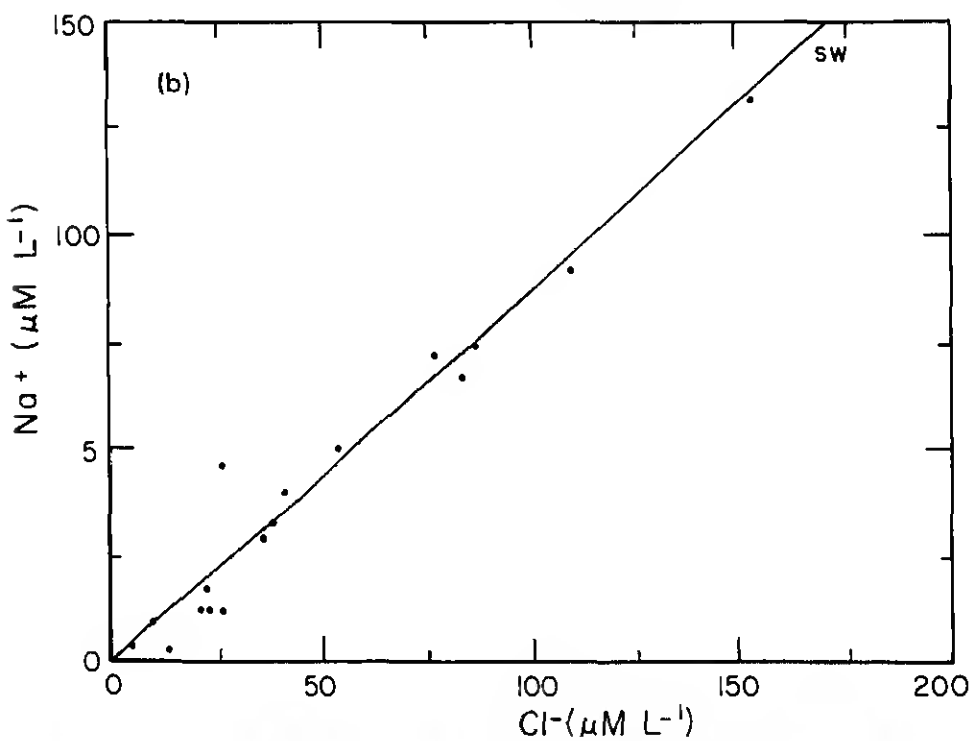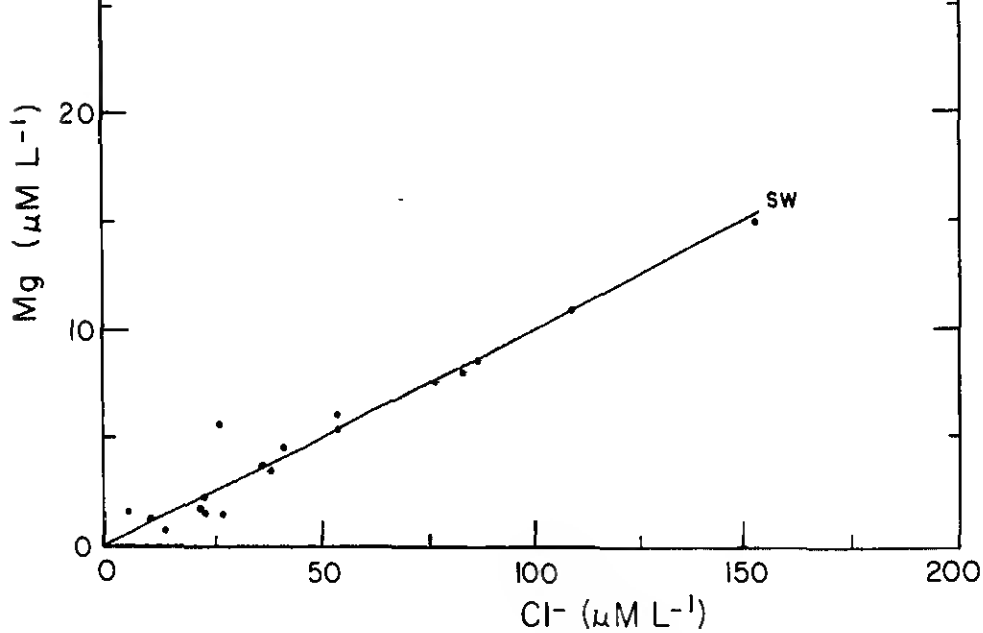
FIGURE 6.13. Chloride versus Mg^{++}(a) and Na^+(b) for Lewes rain. The
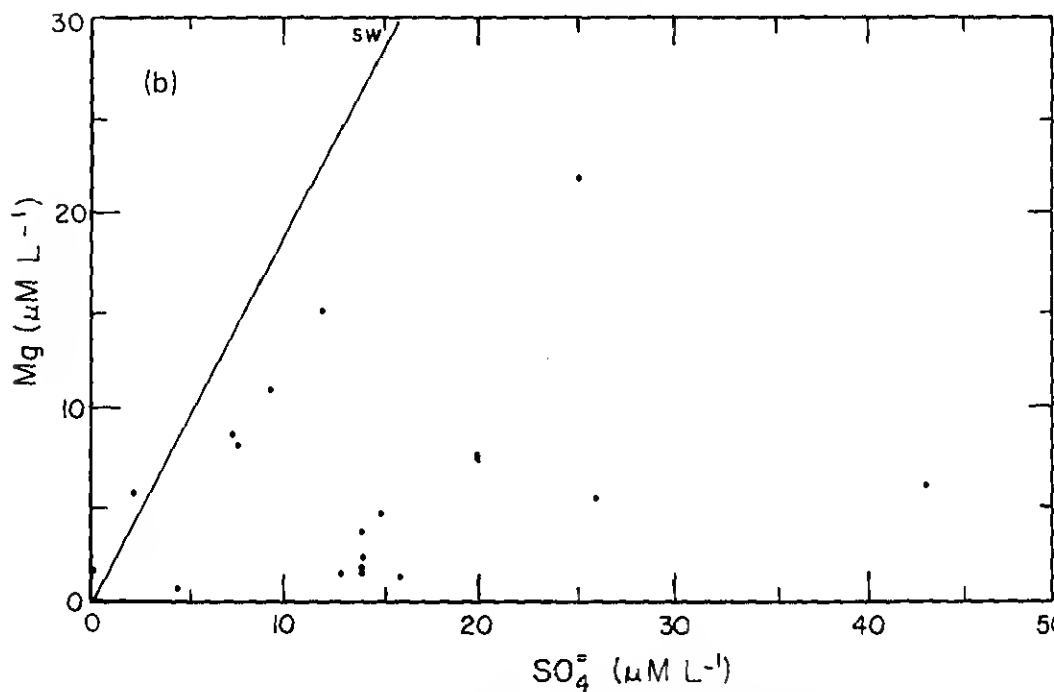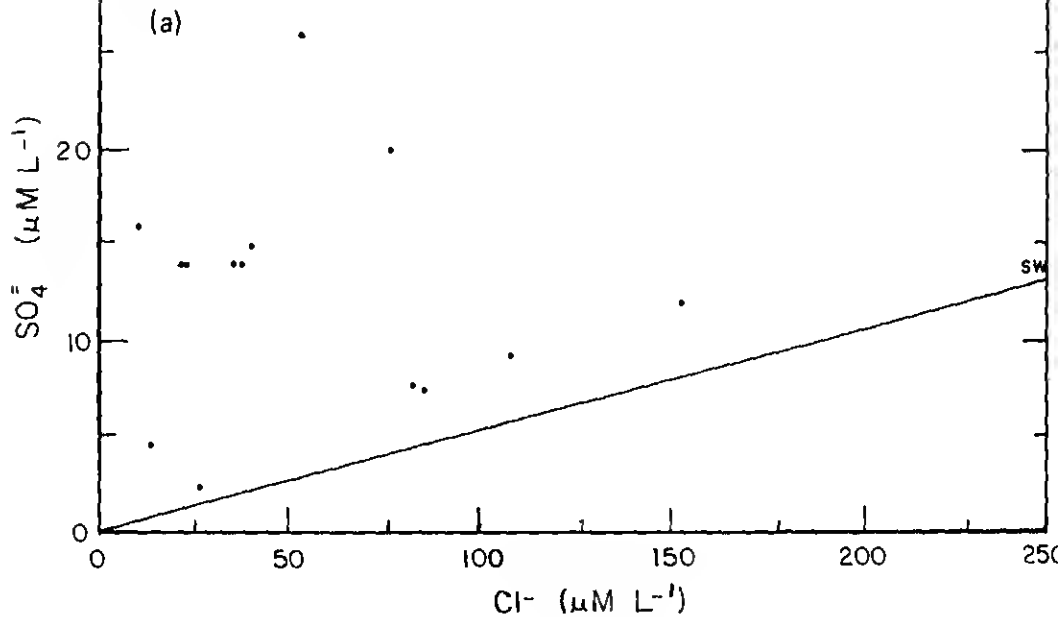
FIGURE 6.14 Sulfate versus chloride (a) and magnesium (b) in Lewes rain. The solid line represents sea salt proportions.

It is evident that sulfate goes through a pronounced seasonal cycle which, like the acidity of the rain, peaks in the summer and decreases the summer months (as do other MAP3S sites). Nitrate also seems follow this pattern, but to a lesser degree. The relative contribution sulfate to nitrate reaches maxima in winter and summer months, li
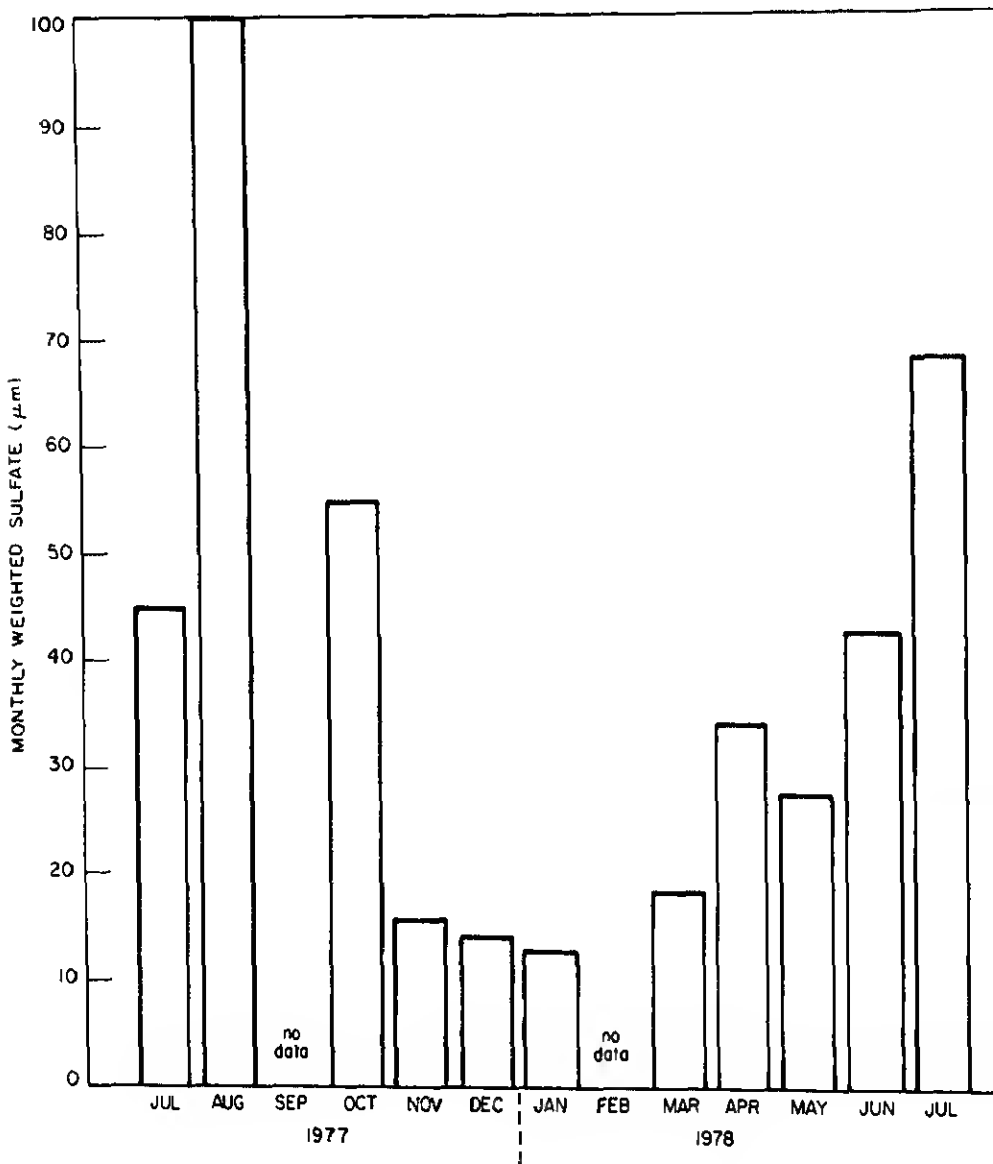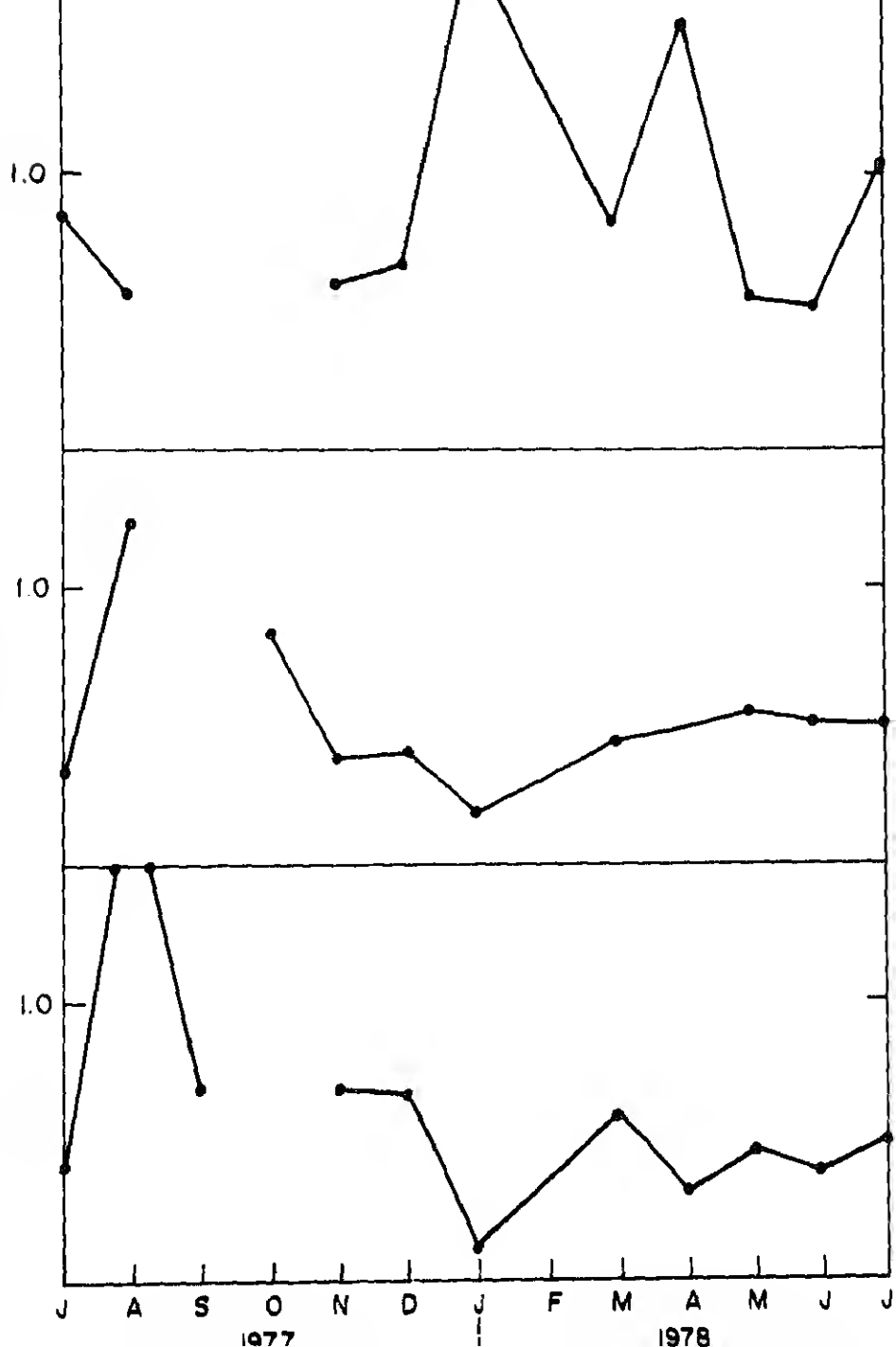
about equal. These observations and seasonal trends are consistent with previous investigations of acid rain components with the highest concentrations and oxidation rates for fossil fuel sulfur occurring in the summer.

It has been suggested by Fisher (1968) that some of the acidity in rain may be neutralized by interaction with calcium mineral nuclei, and that one way to test this hypothesis is to plot the proton concentration against the difference between sulfate and calcium when sulfate is in excess. This format is used to plot Lewes rain water in Fig. 6.17. A
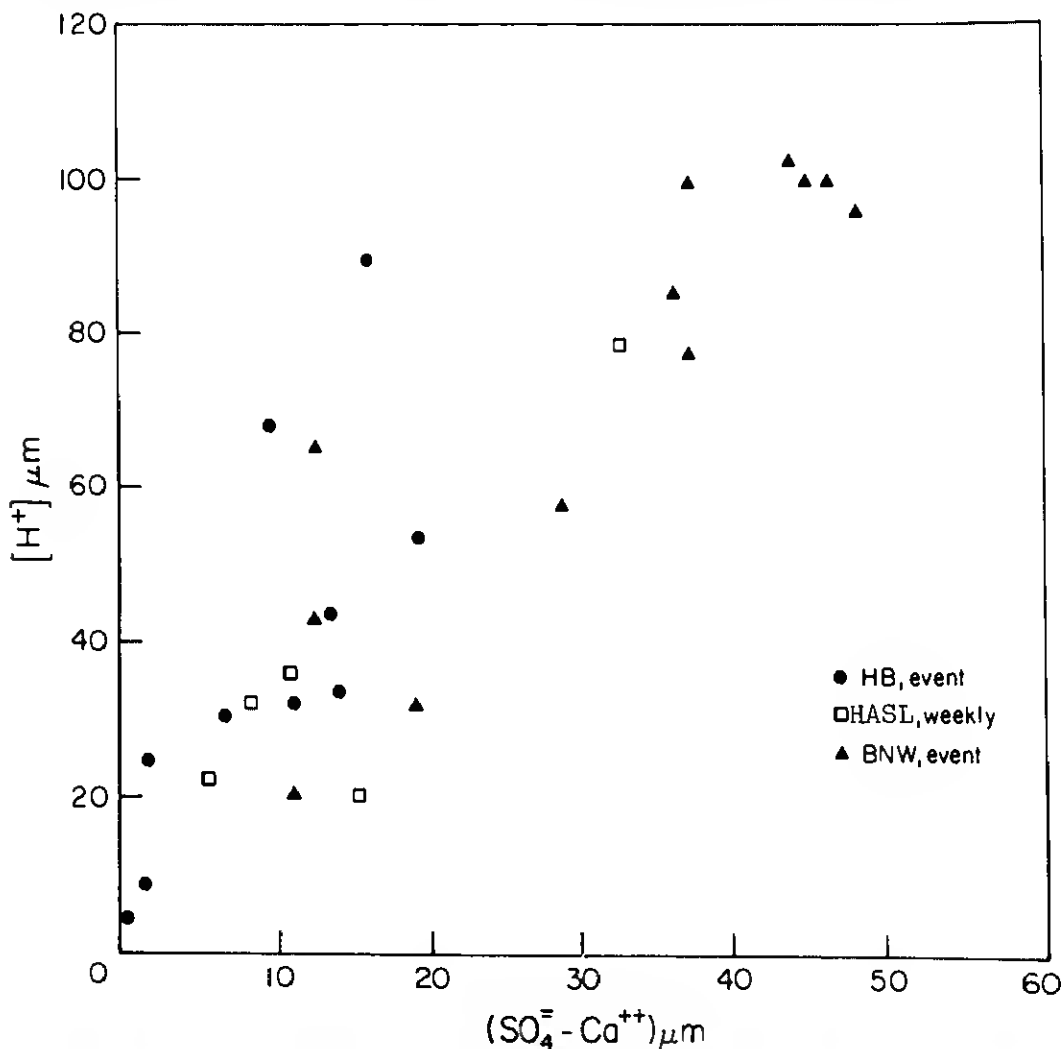
FIGURE 6.17 Hydrogen ion concentration versus non-neutralized com-

tool for assessing the dry aerosol neutralization of acid rain by dust components versus cation contributions from sea salt as calculated from the chloride contributions. Because the limestone contributions from local geologies or agricultural use may be more evident at other MAP3S sites, and since most unfiltered MAP3S samples will probably show this relationship to some degree, this type of analysis needs to be carried out for other sites, too.

6.4.6.3 A Sulfur Flux Calculation of Lewes Rain

Using the available data, an assessment can be made of the potential contributions to the rain sulfur budget at Lewes, Delaware. The monthly weighted mean annual sulfate (non-sea salt) concentration of rain falling between July 1977 and 1978 at the Lewes MAP3S site was $39 \mu m$ or a wet deposition rate of 12.8 kg S/ha/yr. Almost 200 km directly to the west at College Park, Maryland, Muhlbaier (1978) observed a mean sulfate rain concentration of $31 \mu m$ in 1975-1976, or 10.1 kg S/ha/yr. Although these two fluxes compare well, apparently Lewes could receive an excess of about +2.7 kg S/ha/yr if it is assumed that the rain falling at College Park in 1975-1976 is typical of the source rain traveling east across the Delmarva peninsula and falling at Lewes in 1977-1978. Since the Delmarva peninsula is a sparsely populated rural area typified by flat terrain and tidal wetlands, a reasonable source for such excess non-sea salt sulfur in Lewes rain might be biogenic reduced sulfides degassing from the surfaces of salt marshes. In August 1978, as part of a coordinated EPRI MAP3S project at Lewes, Dr. Don Adams (personal communication), of Washington State University, measured a total gaseous sulfur flux from a Lewes high marsh of 3 g S/m^2/yr as a maximum. (The range of fluxes was considerable with a minimum of 0.05 for low intertidal areas and mean of 0.5 g S/m^2/yr. However, the maximum compares well with maximum fluxes in high marshes in North and South Carolina of 3-6 g S/m^2/yr.) If Delmarva high marshes, which occupy about 1.3×10^5 ha, have the same maximum flux of gaseous sulfur, and all of this were rained out as sulfate on the peninsula, then the rain at Lewes could inherit a maximum of +2.5 kg S/ha/yr of excess sulfur. This agrees well with the observed excess. This calculation is presented as a scenario in Fig. 6.18.

There are several reasons, however, why this is an unreasonably high estimate of the excess non-sea salt sulfate that might be inherited by Lewes rain. Much of the degassed sulfur, even if rapidly oxidized to sulfate, should be exported within a day out of the Delmarva area. This is faster than most rain out events. Further, it is also unreasonable to assume that rapid oxidation occurs, since hydrogen sulfide oxidation could take days (Graedel, 1978). More important, it appears that most of
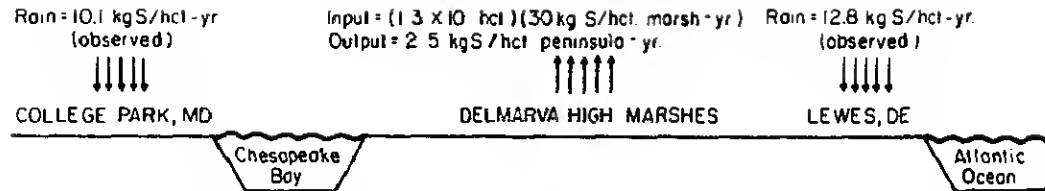
FIGURE 6.18 Simplified diagram of potential biogenic sulfur contributions to sulfur budget of rains moving across the Delmarva Peninsula to the MAP3S site at Lewes, DE.

communication). According to Graedel (1978) such species should have lifetimes of months to years. Thus, it is unlikely that biogenic sulfur emissions from salt marshes would be oxidized to rain sulfate in the short term of days under local meteorological conditions. Nonetheless, there should be much greater research to detail the fate of carbon sulfide emissions from tidal wet lands on the rain water sulfite budget of marine areas and the global atmospheric sulfur budget in general.

6.4.7 Sulfur Deposition in the Eastern United States

6.4.7.1 Introduction

Sulfur is transferred from the atmosphere to the lithosphere and hydrosphere by wet and dry deposition. Although these processes have occurred throughout geologic time, recently the rate of deposition has increased substantially due to combustion of fossil fuels. This section discusses the phenomenon of this increase by investigating the temporal and spatial trends of sulfur in wet deposition in the eastern United States.

6.4.7.2 Natural Rates of Sulfur Deposition

To assess changes in the rate of sulfur deposition, it is necessary to have baseline data from the area of concern before it was disturbed by anthropogenic activities. In the eastern United States man has probably had a significant effect on the composition of precipitation since the early 19th century. However, earliest continuous records of precipitation composition extend back to only 1915 (Likens, 1972). Therefore, a determination of natural deposition rates for the eastern United States is not possible. There are two alternatives: first, current sulfur deposition rates in unperturbed areas can be compiled and assumptions made relative to the comparability of the areas to the eastern United States; second, the historical records of precipitation composition contained in permanent glaciers can be examined.

precipitation. Therefore, for the eastern United States a maximum estimate of the natural rate of sulfur deposition would be about 1 kg/ha/yr. Since the current rate of sulfur deposition in the eastern United States is between 8 and 15 kg/ha/yr (depending on location and precipitation amount), it is probably a factor of at least 5 over the value of the last 200 years. This conclusion is supported by an analysis of the historical record of sulfur deposition contained in the South Greenland permanent ice sheet. Koide and Goldberg (1971) and Weiss et al. (1974) report that the sulfur concentrations in the ice sheet have increased by about 3 times since the first half of the 20th century. Since this increase is related to the increased use of fossil fuels in the United States and Canada it is a reasonable assumption that increases in sulfur deposition in the eastern United States were greater than those observed in Greenland. Therefore, the limited ice sheet data available appears to conform that over the last 200 years sulfur deposition in the eastern United States has probably increased by at least a factor of 5.

As mentioned previously, the longest continuous record of precipitation composition in the eastern United States exists for Ithaca, New York where records of sulfur and nitrogen deposition have been kept from 1915 to 1977 (Fig. 6.19). Although this record is not suitable for the determination of natural deposition rates, it is usable for the determination of changes in the anthropogenic influence on sulfur and nitrogen deposition. The observed decrease in $SO_4^=$ and steady increase in NO_3^- in precipitation is due to a shift from coal to natural gas as fuels for home furnaces. This record is in no way indicative of a regional pattern as it is complicated by the fact that the local use of coal probably heavily influenced the precipitation composition and therefore it is difficult to make any statements as to regional trends.

To understand changes in sulfur deposition on a regional basis, it is necessary to investigate data from sites removed from local sources. Over the past 25 years there have been a few such studies. Figures 6.20 and 6.21 are compilations of these data for the concentration of sulfur and the deposition of sulfur in precipitation, respectively. Note that:

- Current deposition of sulfur (Fig. 6.21) is large relative to estimates of the natural deposition rate (1 kg/ha/yr).

- Relative to temporal trends, there are no identifiable patterns from 1955-1977 (Figs 6.20 and 6.21).

- In 1977, there was substantial variation in the precipitation concentration and deposition of sulfur. This is related to two
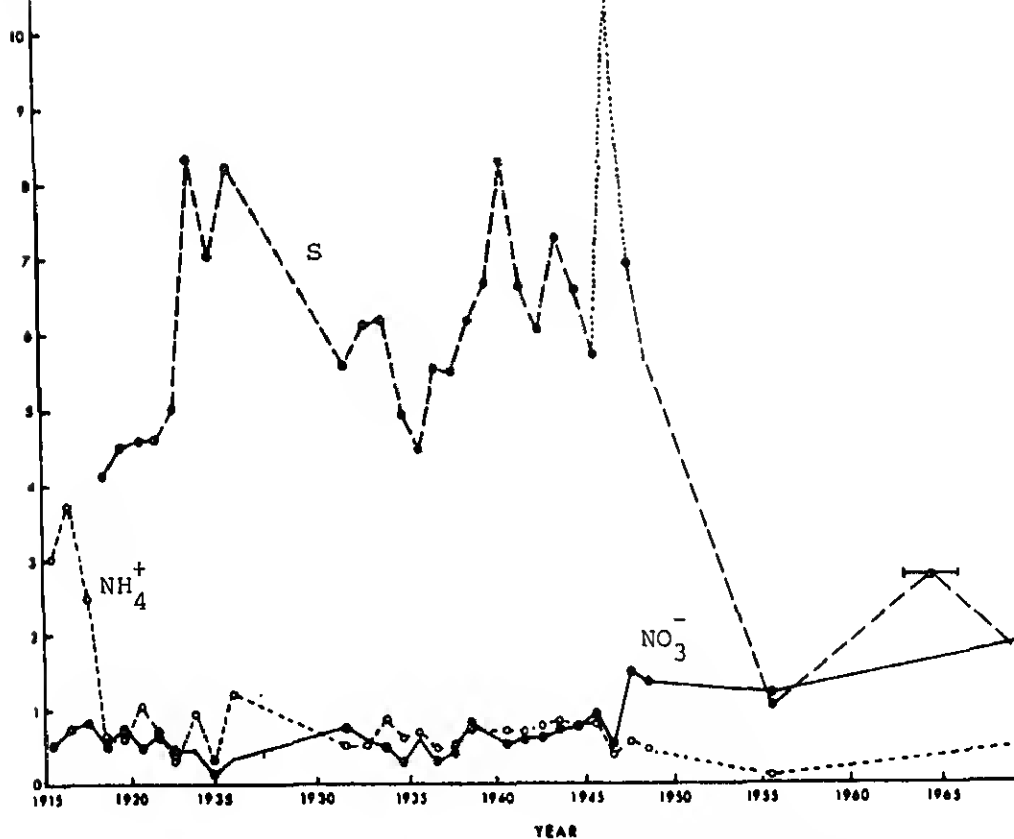
FIGURE 6.19 Weighted annual concentrations of S ($SO_4^=$-S), NH_4^+ NO_3^- in precipitation in Ithaca, NY (Likens, 1972).

● The current record is not suitable to discern trends in composition of atmospheric deposition. A long term data b over a wide region is required.

The weighted annual concentration of sulfur in precipitation varies about a factor of 2 between Virginia and New Hampshire (Fig. 6. Variability is attributable to differences in precipitation amounts location of sampling sites relative to source areas. In order to be understand the phenomena of anthropogenic sulfur in precipitation i instructive to decrease the temporal scale from years to months. Fig 6.22 presents the volume weighted $SO_4^=$ concentration on a mon
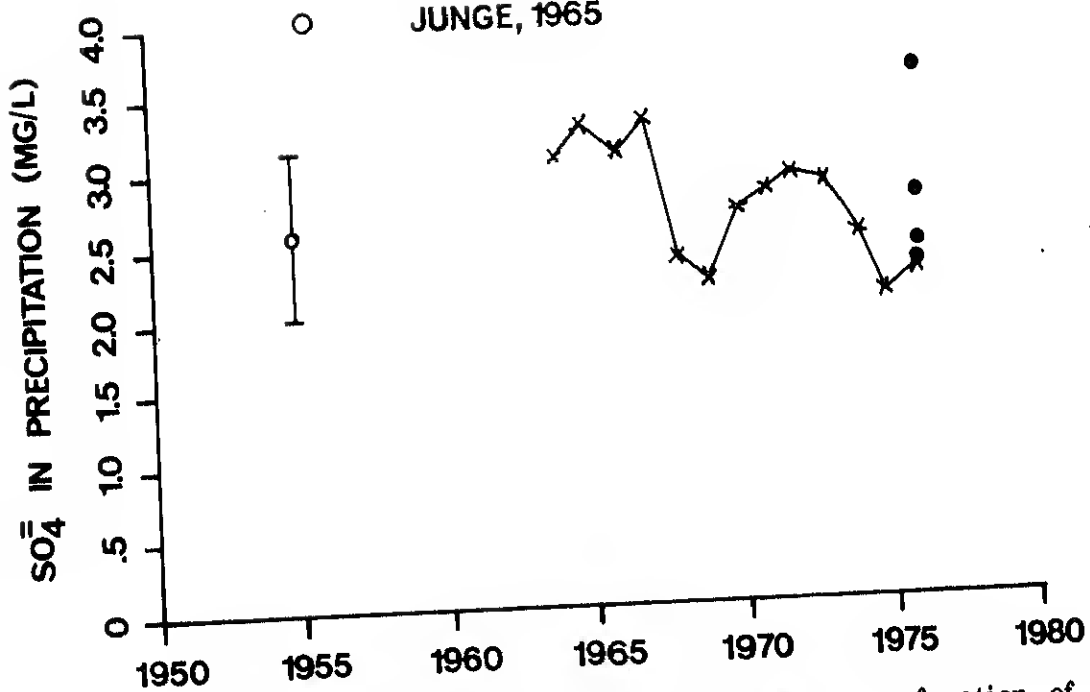
FIGURE 6.20 Annual weighted sulfur concentration as a function of time.

basis for 5 sites in the eastern United States for 1976/1977.[*] The following points can be made.

- $SO_4^=$ concentrations have a summer maximum at all sites. This is believed to be caused by a higher emission rate of sulfur into the atmosphere in the summer and a faster rate of oxidation of SO_2 to sulfate due to higher temperature and humidity.

- Hubbard Brook and Whiteface Mountain have significantly smaller summer maxima. This may be due to temperature, location of source regions and precipitation amount.

- Monthly $SO_4^=$ concentrations in precipitation are remarkably constant in Virginia, Pennsylvania and Ithaca, New York. This

*This figure used some preliminary MAP3S data in developing monthly averages for 1976 and early 1977. This does not qualitatively change the results.
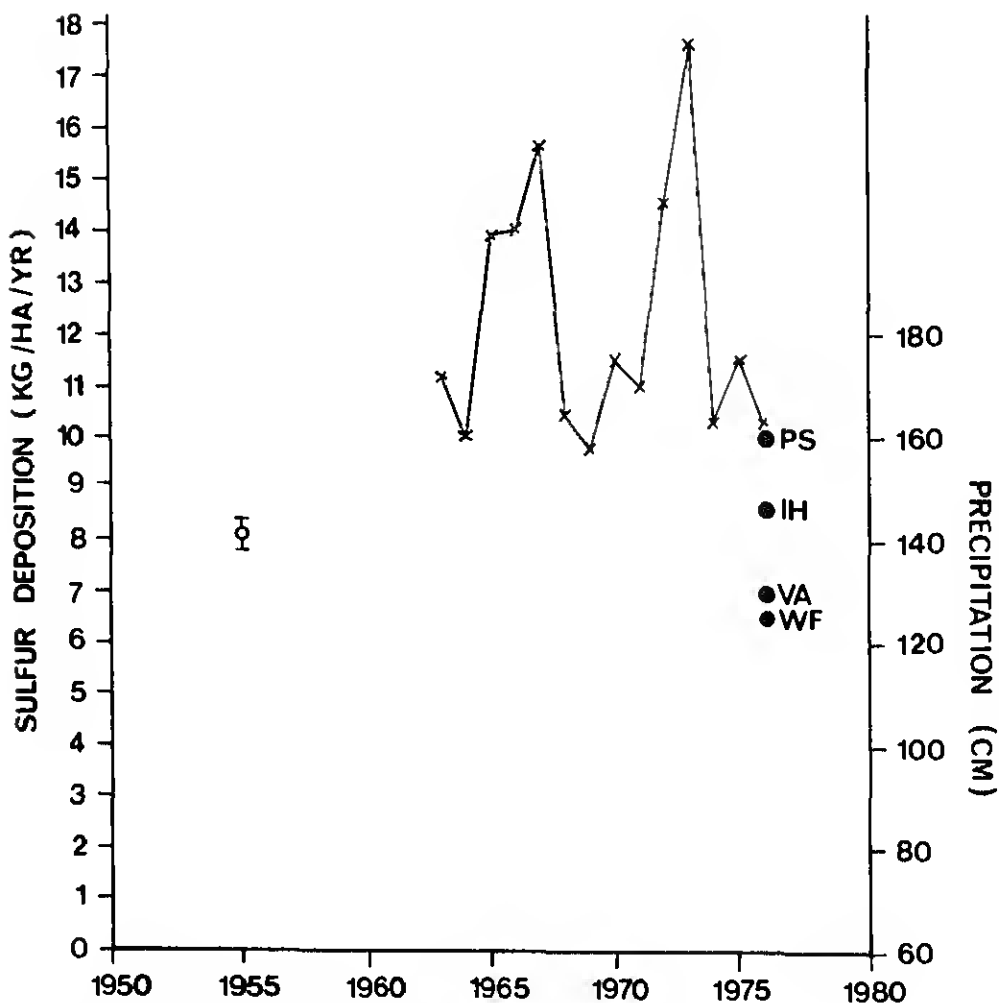
FIGURE 6.21   Sulfur deposition as a function of time.

suggests a high degree of atmospheric mixing over a monthly time scale.

Geographical variations in the composition of precipitation are difficult to determine, again due to the lack of a suitable data base. To
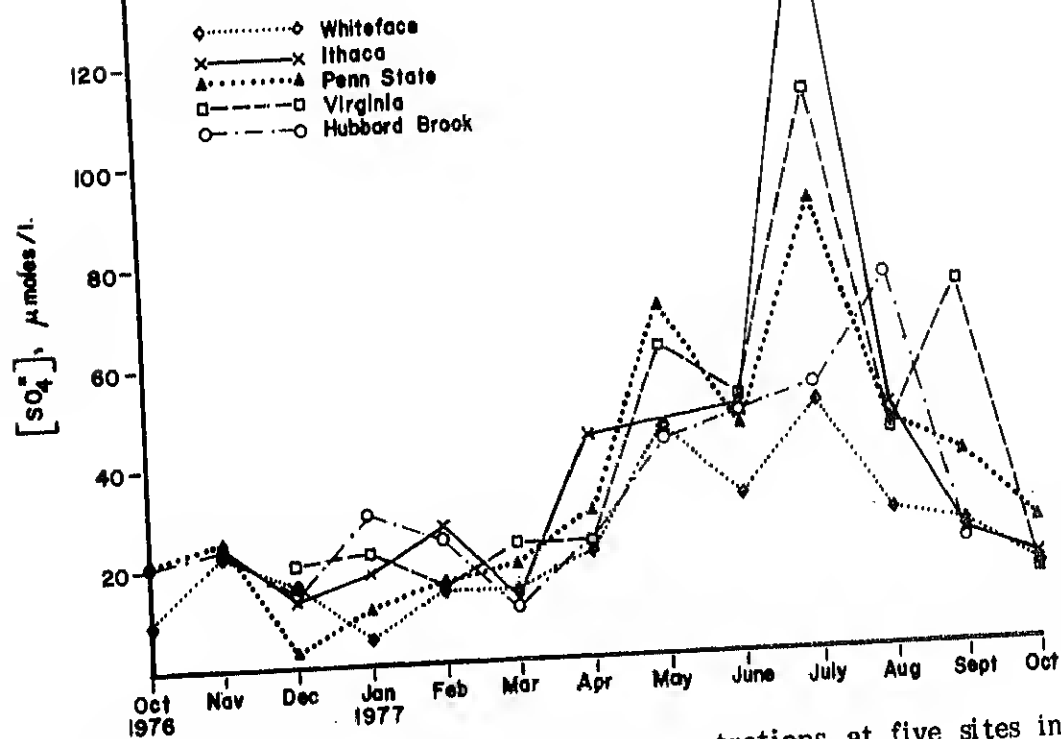
FIGURE 6.22 Weighted monthly sulfate concentrations at five sites in eastern United States.

precipitation during 1977 were contacted* and their data were added to the data from the MAP3S network. This enabled the construction of a map of sulfur in precipitation for 1977 (Galloway and Whelpdale, 1979). A compilation of these published and unpublished data on sulfur deposition in Fig. 6.23 shows no apparent geographical trends in the eastern United States. One reason for this is that differences in collection procedures obscure possible trends. The data fall into two ranges: >11 kg/ha/yr (13 cases) and <11 kg/ha/yr (11 cases); the latter were exclusively from monthly collections while the former were primarily from event or weekly collections. Inefficient collection, sample evaporation, and sample contamination are problems commonly
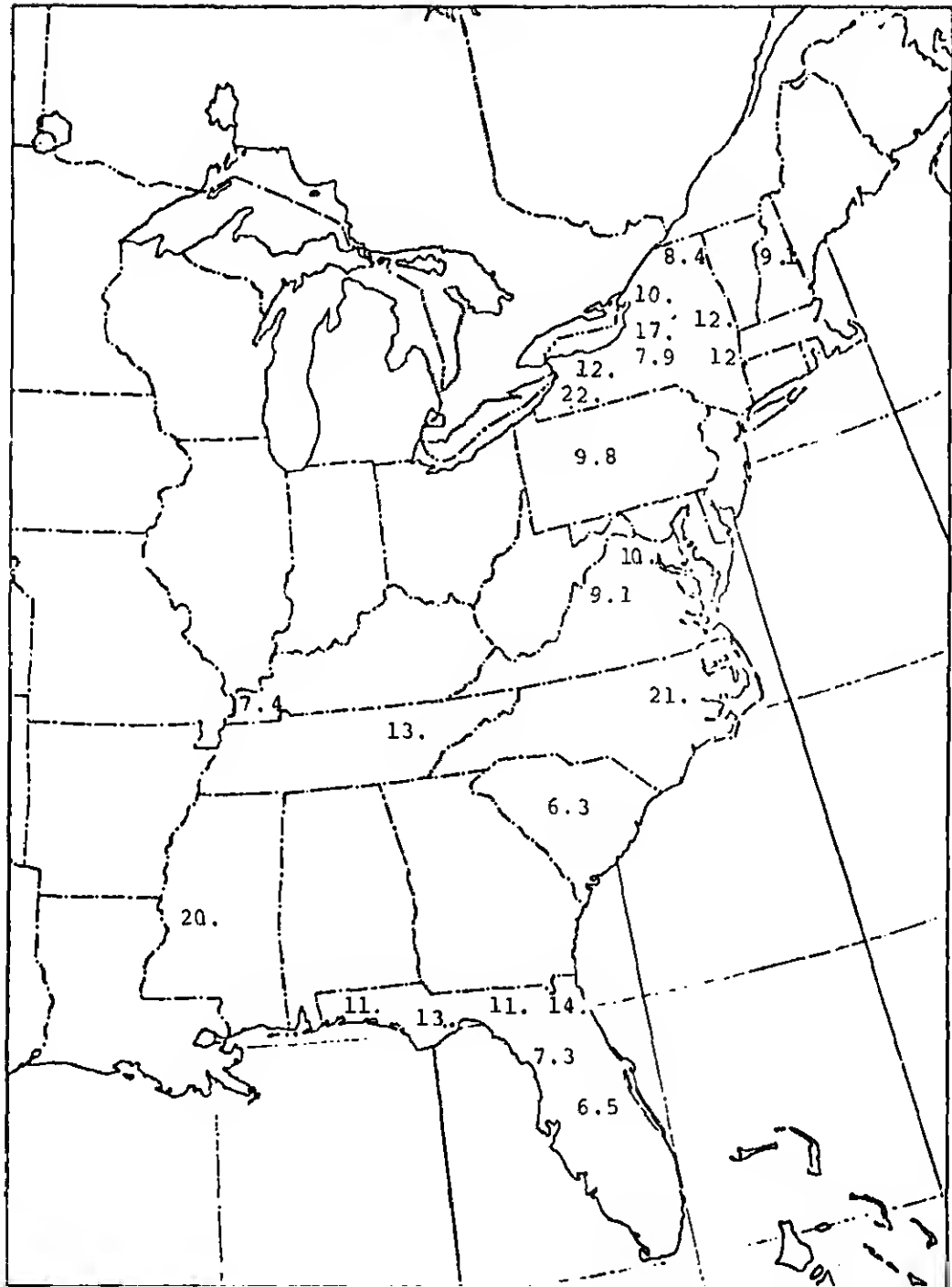
(Galloway and Likens, 1976; 1978). Monthly collection the
latter two because the sample is in the field for a longer time and is thus
more susceptible to evaporation and contamination. The monthly U.S.
data may be affected in this way and may therefore give wet deposition
values that are too high. Where there is a basis for comparison (e.g.,
New York State) monthly values are greater (by up to a factor of two)
than event or weekly values.

The average wet deposition in the eastern United States, based on all
24 values is 11.8 ± 4.4 kg/ha/yr. This gives a total deposition for the
eastern United States of 2.5 TgS/yr. On the basis of the discussion
above, we expect that this number is probably high by up to 15%. A
more extensive network using event or weekly sampling is required to
determine this flux more accurately.

From the presented data, it appears that in the eastern United States
the current concentration of sulfur in precipitation and its resultant
deposition is several times higher than existed previously. In addition
this phenomena of increased sulfur in precipitation occurs over most of
the eastern United States and exhibits a summer maximum. From
previous work, it is also known that the increased sulfur in precipitation,
together with increased nitrogen in precipitation, have caused an
increase in precipitation acidity (Likens and Bormann, 1974; Cogbill and
Likens, 1974; Galloway et al., 1976). What is less well known is the exact
contribution of H_2SO_4 versus HNO_3 to precipitation acidity. On a
stoichiometric basis the relative contribution of H_2SO_4 versus HNO_3
varies from 60%/40% to 70%/30%. However, it appears that over the
last ten years the importance of HNO_3 to H_2SO_4 has increased (Likens et
al., 1976; Galloway and Likens, 1977). Recent data show that the
maximum contribution from HNO_3 to the acidity of precipitation varies
on a seasonal basis, with a maximum contribution of about 75% in the
winter and a minimum contribution of about 25% in the summer. This is
calculated by assuming that all of the NO_3^- in precipitation was
originally in the form of HNO_3. Therefore, in the winter, H_2SO_4 can
contribute only about 40-50% of the acidity while the balance comes
from HNO_3. In the summer, HNO_3 can contribute only about 20-30%,
with the remainder caused by H_2SO_4 (Table 6.14).

Another way of analyzing the influence of H_2SO_4 and HNO_3 on
precipitation acidity is to examine the composition of individual storms
over a large area. For the period from which data are available, seven
different storms have been selected that were large enough to cause
precipitation at 3 or 4 of the MAP3S initial sites (Charlottesville, VA;
State College, PA; Ithaca, NY; and Whiteface Mountain, NY). Since the
comparison of the absolute composition of precipitation at several

	NO_3^-/H^+	$SO_4^=/H^+$
December, 1976	.60 ± .07	.63 ± .12
January, 1977	.36 ± .18	.53 ± .11
February, 1977	.64 ± .12	.51 ± .15
March, 1977	.63 ± .12	1.17 ± .36
April, 1977	.45 ± .03	.81 ± .10
May, 1977	.36 ± .03	.91 ± .08
June, 1977	.32 ± .06	.92 ± .07
July, 1977	.23 ± .02	1.01 ± .26
August, 1977	.33 ± .11	.98 ± .25
September, 1977	.33 ± .11	1.00 ± .15
October, 1977	.39 ± .14	.78 ± .10

[+]The ratios are the monthly weighted averages from the four MAP3S precipitation chemistry sites, ± one standard deviation.

[*]After MAP3S (1977, 1978).

$SO_4^=/NO_3^-$, $SO_4^=/H^+$ and NO_3^-/H^+ of single storm systems are plotted as a function of precipitation amounts (Figs. 6.24 to 6.26).

Figure 6.24 shows the $SO_4^=/NO_3^-$ ratio as a function of precipitation amount for seven different storms. The following conclusions can be drawn.

● The magnitude of the $SO_4^=/NO_3^-$ ratio varies substantially as a function of storm. This is presumably due to different origins of the air masses.

● The magnitude of the ratio varies less as a function of site and precipitation amount. This implies a well mixed atmosphere during the storm duration and perhaps similar scavenging mechanisms for $SO_4^=$ and NO_3^-.

Figure 6.25 shows the variation of $SO_4^=/H^+$ as a function of precipitation amount. The following conclusions are evident.

● The $SO_4^=/H^+$ ratios are quite constant as a function of precipitation amount and site. This implies a strong and constant relationship between $SO_4^=$ and H^+ that is independent of air mass source, storm location and intensity.
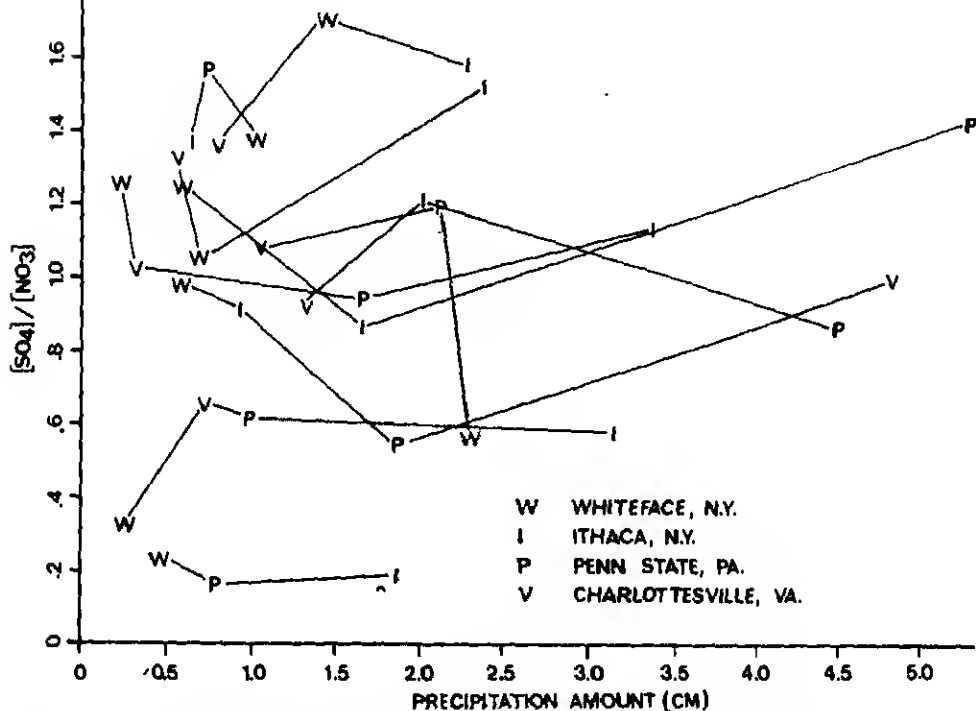
FIGURE 6.24 $SO_4^=/NO_3^-$ in synoptic precipitation as a function of precipitation amount.

- The $SO_4^=/H^+$ molar ratio is remarkably constant within the range of 0.3 and 0.5. This implies that for these seven storms there was enough H_2SO_4 present to account for 60% to 100% of the acidity. Note however, that for one of the storms, H_2SO_4 could only account for < 40% of the acidity.

Figure 6.26 shows the variation of NO_3^-/H^+ as a function of precipitation amount. The variation is significantly greater than for $SO_4^=/H^+$, implying a less strong correlation between H^+ and NO_3^-. However, note that the maximum contribution that HNO_3 could have towards the acidity of precipitation varies from about 35% to 100%. In fact, the one storm where the NO_3^-/H^+ ratio is ~1, is the same storm where the maximum H_2SO_4 contribution to the precipitation acidity was < 40%. Therefore, most of the acidity was due to HNO_3 as opposed to H_2SO_4.

In conclusion, there are four main points.
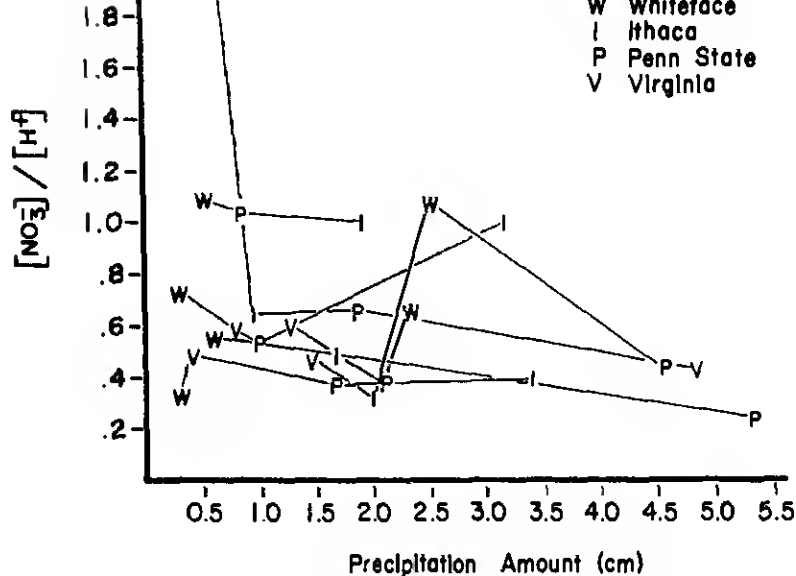
FIGURE 6.25 $SO_4^=/H^+$ in synoptic precipitation as a function of precipitation amount.
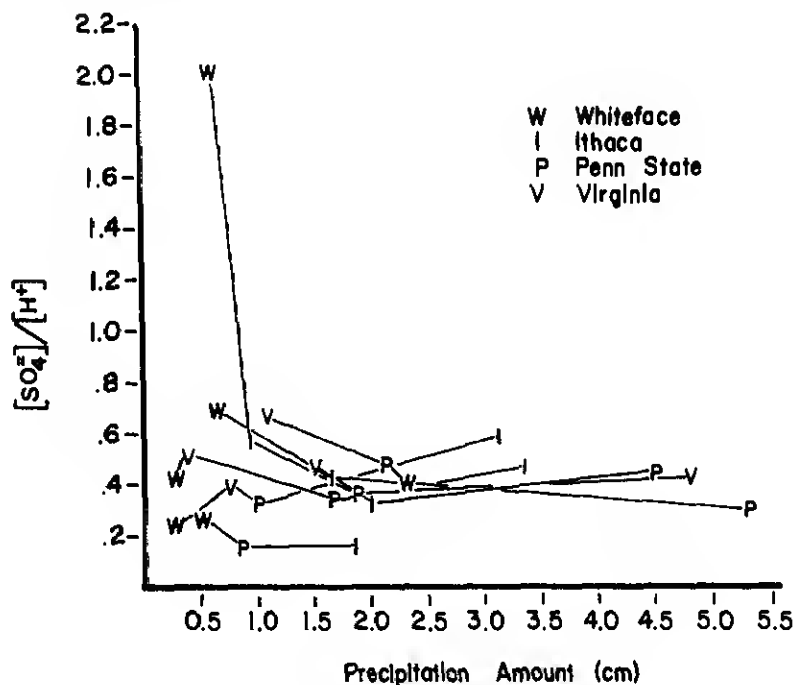
FIGURE 6.26 NO_3^-/H^+ in synoptic precipitation as a function o

3. The increased sulfur in precipitation as H_2SO_4 has caused an acidification of precipitation.

4. Increased precipitation acidity is also due to increased HNO_3 in precipitation. However, at this time, the relative contribution of H_2SO_4 versus HNO_3 is not yet confirmed.

6.4.8 Acid Precipitation Trend in Central Illinois

6.4.8.1 Introduction

The difference in the precipitation chemistry for a rural, east-central Illinois site between 1954 and 1977 was investigated to ascertain whether or not the precipitation became more acidic and if so, why.

The 1954 data set was described in some detail by Stensland (1977), including a comprehensive discussion of the procedure used to calculate the pH from the measured ion concentrations. The value of the measured pH for the 1954 data is not available. The 1954 data set is unique because the manual sampling technique carefully eliminated any dry deposition and because individual precipitation events were sampled. The sampling site in both 1977 and 1954 was at the Champaign-Urbana airport (referred to as CMI). CMI is located 7 kilometers south of Champaign and is surrounded by cultivated fields except for a golf course to the east. The data sets were collected from May 15, 1977 to February 6, 1978, and from October 26, 1953 to August 12, 1954. For convenience the two sets are being referred to as the 1977 data and the 1954 data.

For the 1977 study an automatic wet/dry collector, of the HASL design, was used. Only the results from the wet-side bucket were considered in this analysis. The polyethylene bucket was changed within 24 hours of the end of the precipitation event and then brought immediately to the laboratory where pH and conductivity were measured followed by sample filtration with a 0.45 micrometer membrane filter. The ions $SO_4^=$, NO_3^-, Cl^-, NH_4^+, Ca^{++}, Mg^{++}, K^+, and Na^+ were determined by standard methods on AutoAnalyzer and atomic absorption units.

6.4.8.2 Results

From about May 15 to September 30 the landscape around CMI is mostly gree due to the corn and soybean crops. In the fall season most of the farmland is tilled to produce a brown landscape. Since the local dust conditions may thus be quite different for the two periods, the precipitation chemistry data for 1977 was divided into the green period

Three other data separations are illustrated in the figures. First, in the 1954 data there were six events where consecutive samples were taken and a volume-weighted average was computed for each ion. These average values were used in subsequent analyses. Secondly, there were six events also in the 1954 data where the sample collection began after the precipitation was started. Because the chemical concentrations are highest at the beginning of precipitation events, these six samples were given a special symbol on the figures. Thirdly, for the 1977 samples the procedures allowed very small samples to be analyzed and these data were also denoted by special symbols (see Fig. 6.27). The numbers in parentheses on Figs. 6.27-6.30 indicate the number of events used to obtain the median values.

The frequency distributions of the calculated pH for 1954 and for the measured pH for 1977 are presented in Fig. 6.27. It can be seen that the median pH does not change significantly when the smaller samples are included, but the green period is lower than the brown period pH.

The 1977 combined brown and green period median pH, for events >0.70 mm, is 4.1. This compares with the calculated median pH of 5.9 for the 1954 data. If those 1954 samples with precipitation beginning before collection started are excluded, the 1954 median pH is 6.05. The more basic precipitation in 1954 could have resulted from low levels of acidic ions (e.g., sulfate and nitrate) or from high levels of basic ions (e.g., calcium and magnesium). This issue is addressed on Figs. 6.28 to 6.30. For these figures the small rainfall samples (< 0.70 mm) were not included.

The sulfate data are presented in Fig. 6.28. The median for the 1977 green period was 80 µeq/l, and 65 µeq/l for the brown period. The median for 1954 was 50 µeq/l, but when samples with precipitation prior to the beginning of collection are excluded the 1954 median is 60 µeq/l. For later calculations, the median value of 60 µeq/l is assumed for 1954 while for 1977 a value for the combined green and brown periods of 70 µeq/l is assumed.

The nitrate data are presented in Fig. 6.29. As with sulfate, the 1977 nitrate values had a larger median for the brown period. The median nitrate value for 1977 for the combined brown and green periods was 30 µeq/l. For the individual brown and green periods the median values were 38 µeq/l and 28 µeq/l, respectively. The 1954 median nitrate value was 18 µeq/l, while the exclusion of samples with rain prior to the beginning of collection increases the median to 20 µeq/l.
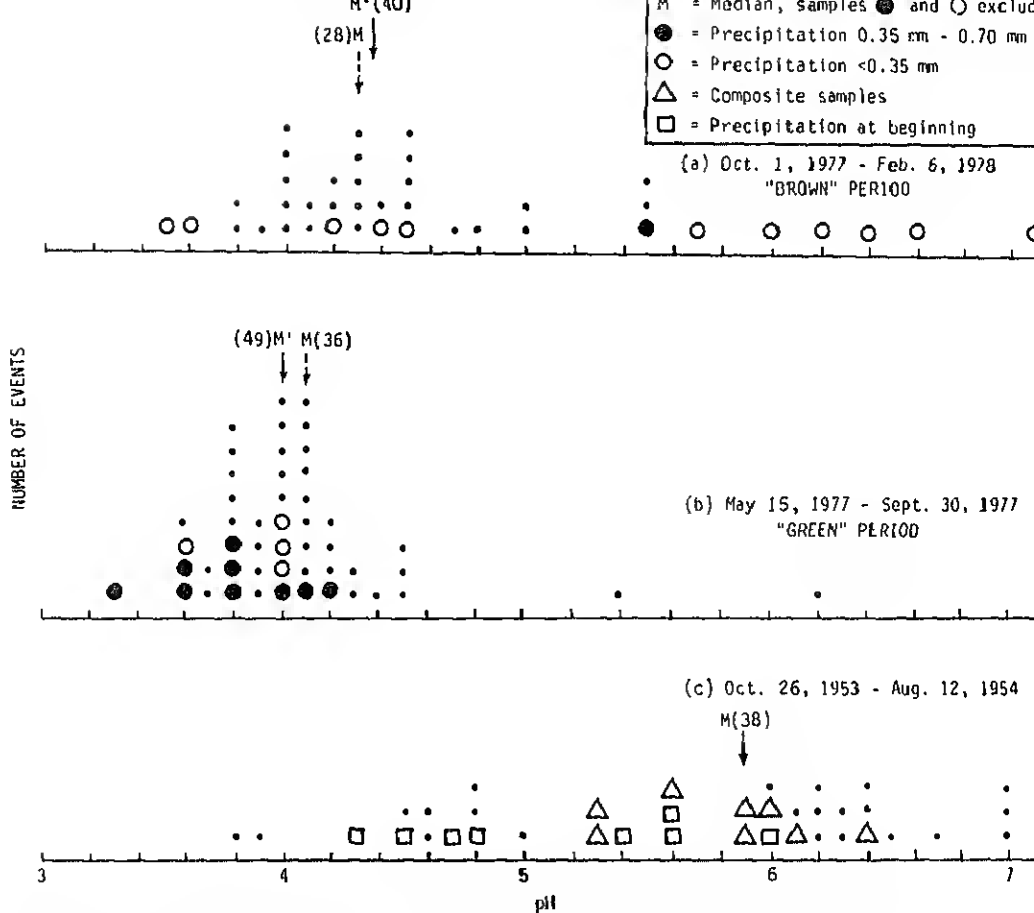
FIGURE 6.27 Frequency distribution of measured pH for 1977 and calculated pH for 1954 precipitation events.

6.30, the data for hardness are presented. The median hardness value for the combined green and brown period was $10 \mu eq/l$. For 1954, the median hardness value was $65 \mu eq/l$, but when samples with rain prior to the beginning of collection are excluded, the median was $82 \mu eq/l$. Of the nine 1954 events with hardness greater than $100 \mu eq/l$, two were in the green period and seven in the brown period.

6.4.8.3 Discussion

With these data, there can be little question that the samples in 1954 were much more basic than the 1977 samples. Although both $SO_4^=$ and NO_3^- were apparently lower in the .1954 samples, it was the high level
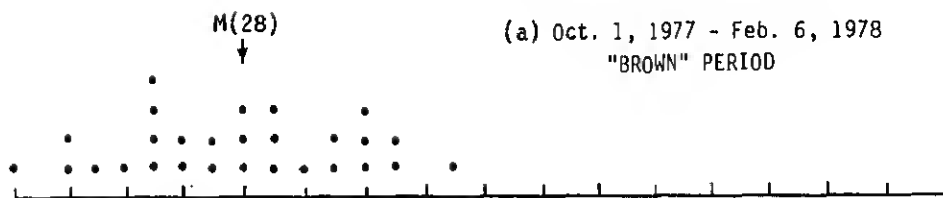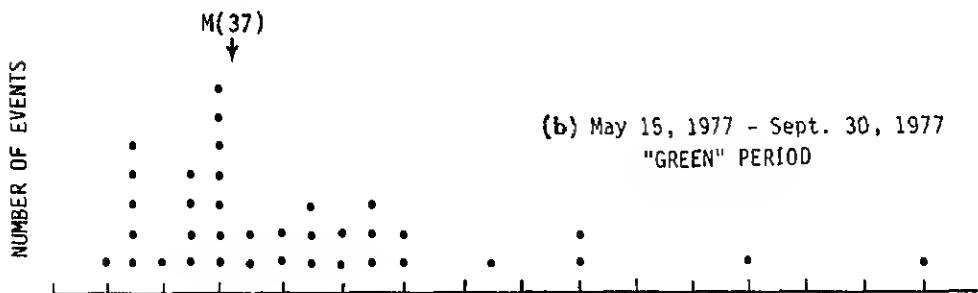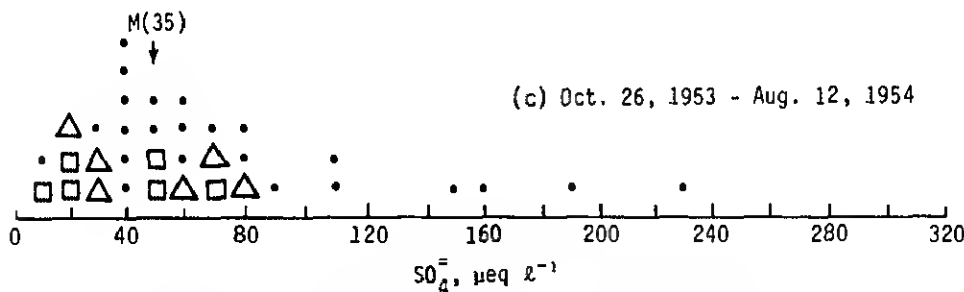
FIGURE 6.28 Frequency distribution of sulfate for 1954 and 1977 precipitation events.

level), the pH would have been 4.18 instead of 5.9. The median pH = 5.9 for 1954 includes the empirical correction discussed by Stensland (1977). Without this correction the 1954 median pH value would have been about 6.6, and 4.28 with the 1977 level of $Ca^{++} + Mg^{++}$.

The high 1954 $Ca^{++} + Mg^{++}$ concentrations could have resulted from either problems in the chemical analysis procedures or they may be indicative of higher ambient air levels of these elements in 1954. Recent work at the ISWS has shown that the $Ca^{++} + Mg^{++}$ levels in rain can rise
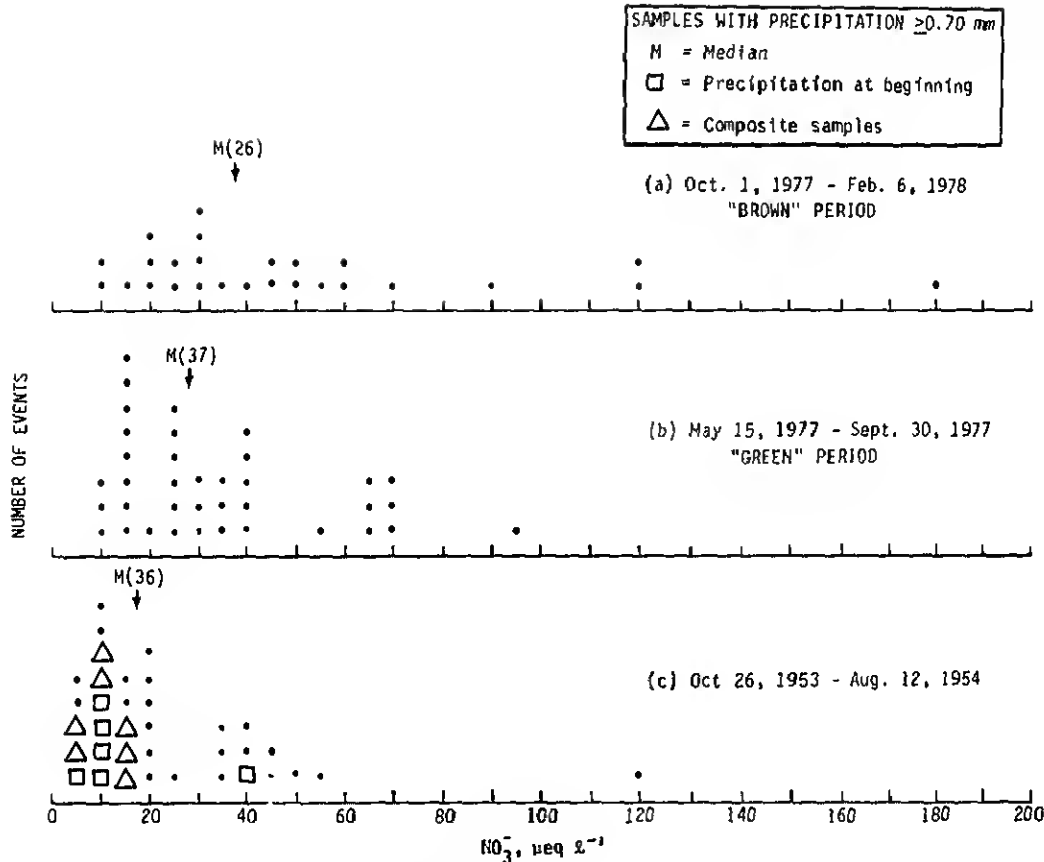
FIGURE 6.29 Frequency distribution of nitrate for 1954 and 1977 precipitation events.

suggest that the absence of filtering will not account for the majority of the increase in the 1954 pH levels compared to the 1977 values.

Assuming now that the reported $Ca^{++} + Mg^{++}$ values accurately represented the precipitation falling in 1954, one must then conclude that more calcium and magnesium were present in the atmospheric aerosols in 1954 than in 1977. A possible source could have been the dust from rural gravel roads. However, a scientist living in the area since 1954 has expressed to this author the feeling that most of the rural roads in the area had an asphalt type surface in 1954, just as they do today, such that the roads would not have been a greater dust source in 1954.
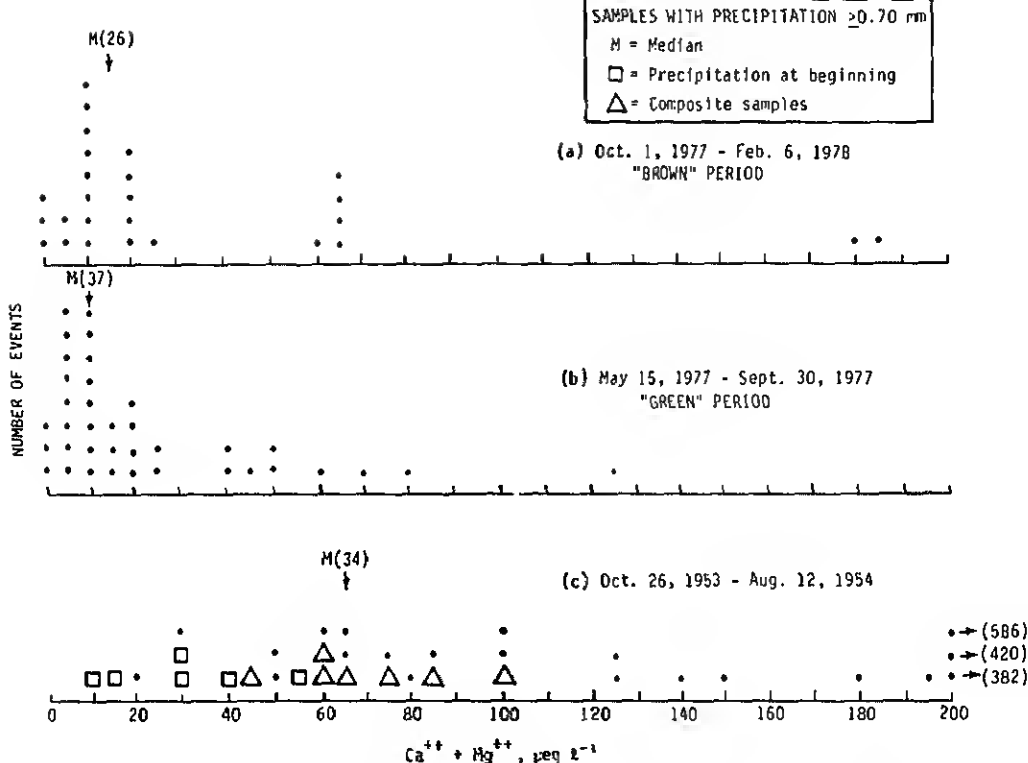
FIGURE 6.30 Frequency distribution of the sum of calcium and magnesium (hardness) for 1954 and 1977 precipitation events.

have modified the local dust levels to some extent, but no quantitative assessment is available. The final suggestion offered for the elevated $Ca^{++} + Mg^{++}$ levels in the atmospheric aerosols is that the years 1953-1954 were very dry in many states of the Midwest and the Plains, and thus more susceptible to wind soil erosion as compared to 1977. For ~~~~~recipitation was -33% (below normal) in Oklahoma, ~~~~~~< for Nebraska, -13% for Missouri, +9% for Iowa, ~~~~~~~~Research is now in progress to more fully ~~~~~~~~~relation between droughts and elevated basic

6.4.9 Seasonal Trends in Precipitation Composition

Monthly mean deposition-weighted concentrations have been calculated for the major ionic species measured in MAP3S network samples. There are approximately two years' data from the first four

report (MAP3S, 1979). As has been noted elsewhere, $SO_4^=$ concentrations reach a maximum in the summertime (July 1977, June 1978) at most sites; the free H^+ concentrations follow the $SO_4^=$ closely, and are approximately equivalent ($SO_4^= \approx 2H^+$) during the warm season. NH_4^+ and NO_3^- concentrations are quite uniform throughout the year, but $SO_4^=$ reaches a minimum, below the NO_3^- average level in the winter. Monthly mean concentrations should be interpreted with care, especially with only two years record, as some seasons and/or months included may be non-typical in terms of precipitation amount or general weather pattern.

Measurements of sulfite (scavenged SO_2) concentration are also being made in order to evaluate the significance of such deposition in the MAP3S region. Aliquots of samples collected at the sites have been chemically fixed to preserve the dissolved SO_2 at the time of sample collection. Data for $SO_3^=$ as well as $SO_4^=$ concentrations are available for the period from October 1977 through June 1978. Figures 6.31 and 5.8 show monthly means of the sulfate concentrations and the fraction of the sulfur in the form of sulfite for this period for three sites. These data are from the PNL and HASL collector samples. Clearly, the cold months show significant fractions of sulfite, but the magnitudes are rather small for both species. An evaluation by ecologists or others interested in biological or surface effects is required before it can be determined whether these levels of sulfite are important enough to warrant continued detailed measurement. As expected from SO_2 solubility theory, sulfite concentrations are quite low in the summertime as precipitation pH decreases and temperature rises. Measurable concentrations of sulfite are rare during the summer, except at Pennsylvania State, where on-site sulfite analyses are conducted as part of the collector intercomparison study (see 6.4.5).

The curves drawn on Fig. 6.32 show the theoretically expected sulfite concentrations in precipitation as a function of precipitation pH and SO_2 air concentrations. Data points from two sites (O - Ithaca, X - Pennsylvania State) show considerable scatter, and because no air concentration measurements accompanied the precipitation collections for this data set, one cannot compare with theory adequately. In addition, many of the samples during this September 1977-January 1978 period were snow samples, thereby modifying the height and temperature at which equilibrium would have occurred. However, it does appear that the sulfite concentrations are of the proper magnitude, and it seems that there is no clear correlation with pH. The PSU collector intercomparison study (see Chapter 6.4.5) will provide a good deal more information about collector efficiencies for sulfite, as well as background data (e.g., SO_2 concentrations in air) for evaluation of the variations.
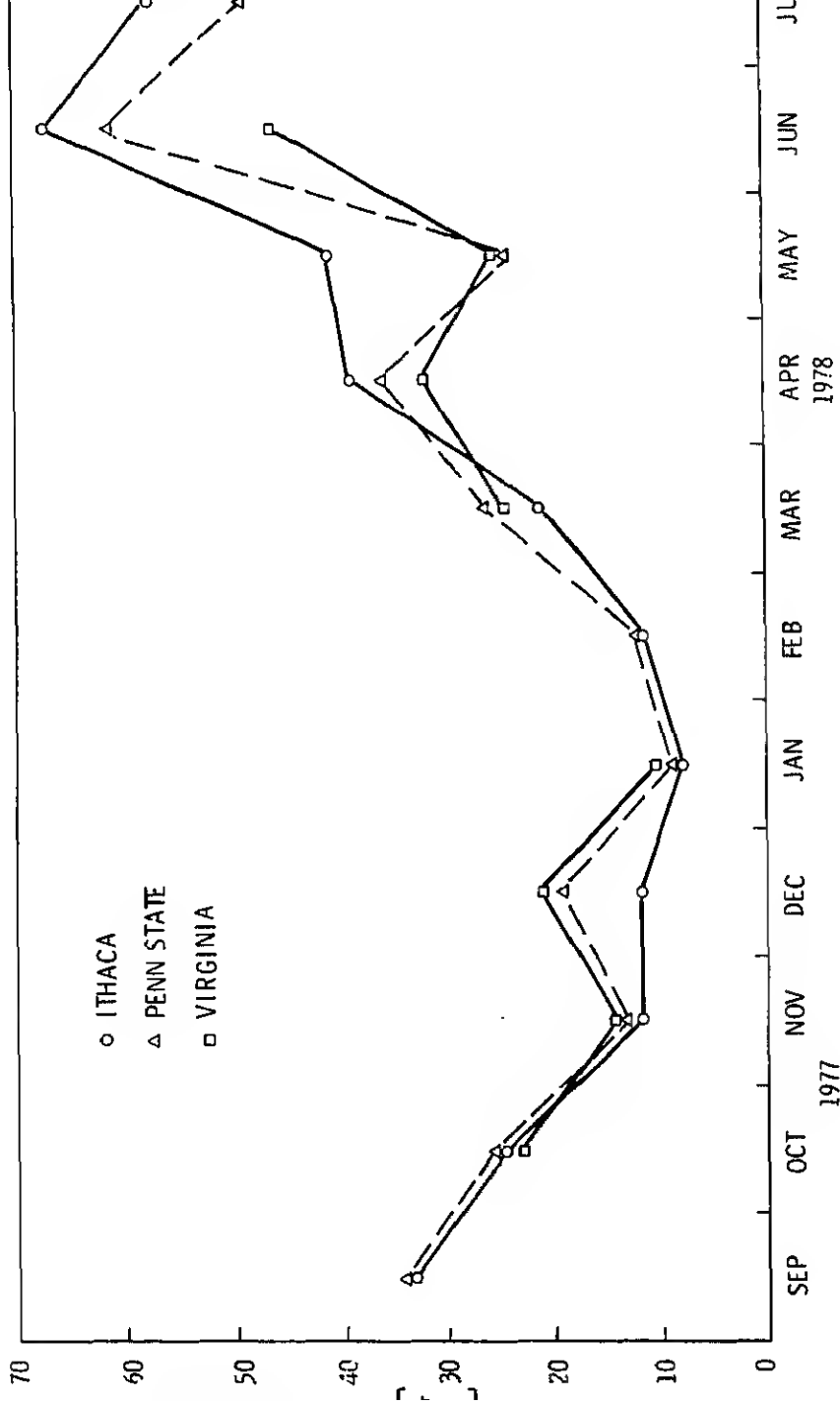
FIGURE 6.31 Monthly mean concentrations of $SO_4^=$ as a function of time at Cornell (Ithaca), PSU, University of Virginia.
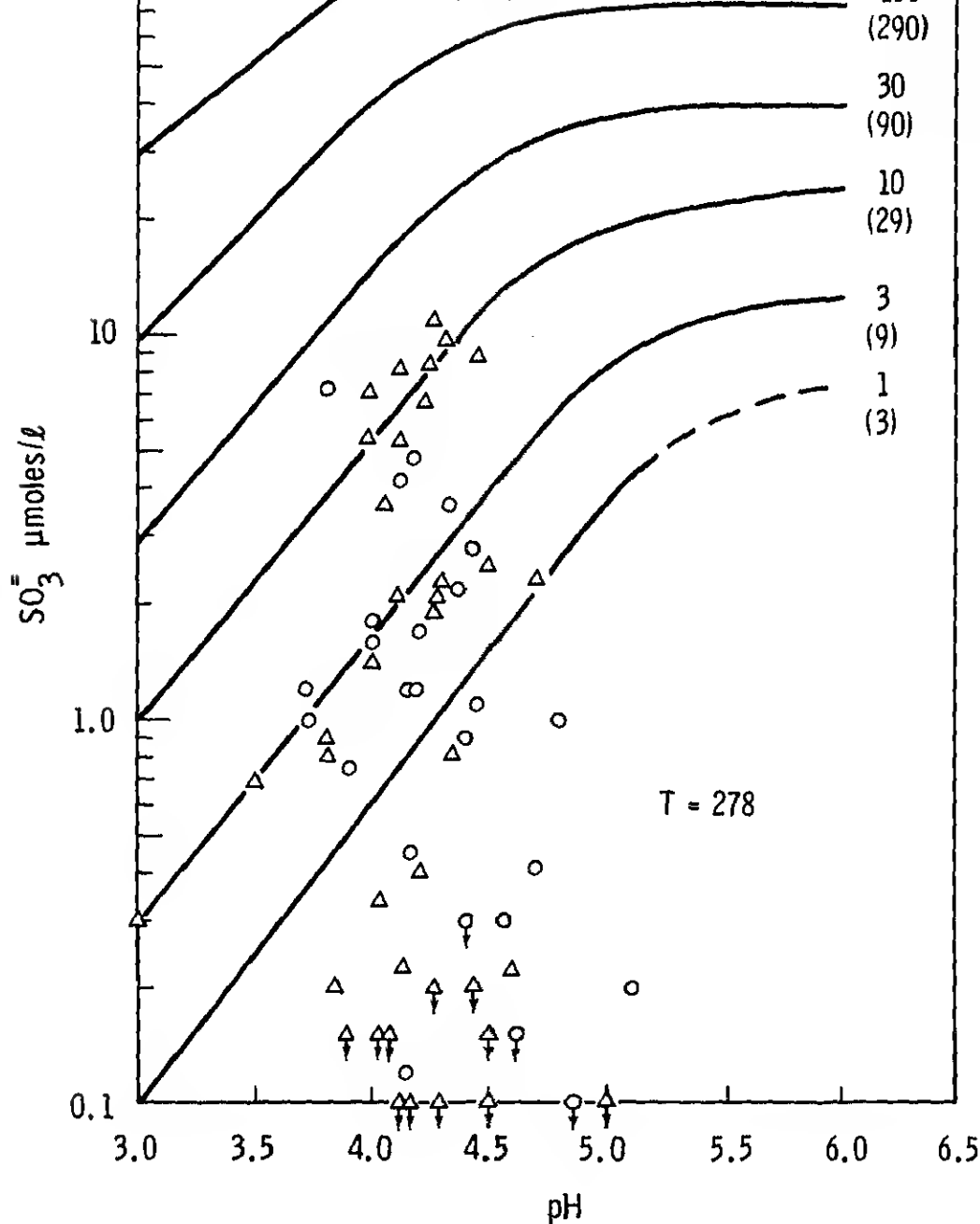
FIGURE 6.32 Solubility of SO₂ in water at 278 K for various concentrations of SO₂ in air (in ppb or in μg/m³ in

Through the initiation of its precipitation chemistry network, MAP3S has helped gather an important (and growing) data base in the northeastern United States. The careful selection of site operators to assure their interest in the data has led to high quality data and extensive complementary and supplementary studies. As a result of studies of the MAP3S data, in the context of other research, it is clear that combustion emissions are affecting the chemistry of precipitation. The major findings to date include the following:

- Current deposition of sulfur (8-15 kg/ha/yr) in the eastern United States is large relative to estimates of the natural deposition rate ($\sim$1 kg/ha/yr).

- Sulfate concentrations in precipitation have a summer maximum, although wintertime concentrations are also substantial. Monthly average sulfate concentrations are remarkably constant over the eastern United States.

- The concentration of nitrate in precipitation is relatively constant over the year, with the maximum relative concentration in winter when it may contribute (on the average) up to half of the acidity.

- The acidity of cloud water may be greater than of rain water, indicating that fogs in mountain areas may have a significant influence on acid deposition.

- There has been a decrease in pH in the midwestern and southern United States over the last twenty years, but this may in part be due to a decrease in the soil component in the collected rain.

- Continued and expanded monitoring of precipitation chemistry is required to better evaluate trends, mechanisms, and ultimately to provide the data base for assessment of effects.

- Collecting precipitation on an event basis is essential if the sources of the pollutants are to be identified through trajectory analyses.

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The disposal of combustion products in the atmosphere depends on dispersion (both horizontally and vertically) to reduce near-source concentrations, and on the efficiency of removal mechanisms to reduce distant concentrations. For point sources with simple physical, topographic, and meteorological conditions and with nonreacting pollutants, the relatively simple Gaussian formulation, employing the well-known Pasquill-Gifford stability classes (Gifford, 1976), has proven reasonably adequate for representing close-range atmospheric effects on pollutant concentrations. For tall stacks, reactive pollutants, complex terrain, light winds, and when vertical layering of the atmosphere is important, however, we need a better understanding of how the atmosphere transports such pollutants and mixes power-plant emissions with pollutants from dispersed sources already present in the air mass.

Studies such as those downwind of St. Louis (e.g., during MISTT, see White et al., 1976; Alkezweeny and Powell, 1977) indicate that, even with contemporary controls on pollutant emissions, cities give rise to palls extending at least 100 km downwind. Early analytic results of the SURE program (Hidy et al., 1976) showed that "The zone of influence of an individual source on the concentration values for the sulfur oxide particulate complex (SPC) appears to be 200 to 300 km weighted toward the downwind direction." Visibility data and inert tracer releases reveal that pollutants can be transported to even longer distances in the lower atmosphere, before dispersion and removal processes reduce concentrations to background levels.

The vertical mixing of pollutants is equally complex. Diurnal changes in atmospheric stability lead to vertical dispersal up to several kilometers altitude during daytime mixing periods. During nighttime, this may lead to the isolation of pollutants aloft, as low level nocturnal inversions are formed (e.g., see Hess and Hicks, 1975). Depending on wind speed and direction, these isolated pollutant layers can be transported long distances during nighttime hours, as evidenced, for example, by results obtained in the flight of a manned balloon (da Vinci Program) in 1976 (Zak, 1976). The pollutants contact the surface again when sufficient subsequent daytime mixing takes place. Vertical motions in nonprecipitating clouds can also mix pollutants higher into the atmosphere, where horizontal wind speed is usually greater.

Although it has long been known that long-distance transport occurs on some occasions, an adequate understanding is lacking of the mechanisms that interact to produce such transport and the parameters that determine whether it will occur under particular conditions.

The MAP3S research plan includes of the horizontal and vertical focus on improving our understanding of the horizontal and vertical processes leading to long-range transport, development and later use of inert tracer capabilities that allow air masses to be followed out to distances up to 1000 km, and model development research intended to improve the present capabilities for estimating air mass flow from limited routine meteorological observations.

7.1 VERTICAL TRANSPORT AND MIXING

The distribution of pollutants in the vertical depends upon a number of meteorological factors, as well as upon the height of injection. In the daytime, for example, industrial emissions will be spread rapidly throughout the mixed layer of the lower atmosphere to a height that is typically 1-2 km. But at night, the lower atmosphere becomes stable, and strongly stratified flow can develop. In summer, nocturnal flow is often effectively decoupled from the surface and winds aloft are free to accelerate to speeds considerably greater than surface observations would indicate, resulting in the transport of pollutants for considerable distances largely unaffected by surface deposition and other terrain considerations.

In the daytime, the height of the well-mixed layer determines the extent to which pollutants are diluted by mixing with cleaner air aloft, while the mixing process itself distributes material uniformly throughout the atmosphere below the capping inversion. At night, the strength of the surface inversion determines the likelihood that air aloft will become decoupled from the constraints imposed by friction at the surface; clearly the height of this inversion must be taken into account in considering the effect of alternative heights of emission.

The evolution of the layer of the atmosphere in which pollutants are mixed, commonly referred to as the planetary boundary layer (PBL), has been addressed as part of several MAP3S field programs and formulations for estimating its behavior are being proposed and tested.

7.1.1 Field Experiments and Observations

An intensive study of the growth of the convective mixing layer was conducted by ANL during the summer of 1975. This was the first of the "Sangamon" experiments, named after the county in central Illinois in which the main field site was located. The Sangamon 1975 study led directly to the first truly cooperative MAP3S field experiment, a study of pollutant behavior associated with the development of the nocturnal inversion conducted by ANL, PNL and ISWS during the summer of 197

have been reported extensively elsewhere (Hicks and Wesely, 1978; Hicks and Sheih, 1977; Sisterson and Frenzen, 1978; Holt et al., 1978; Yamada and Berman, 1979; and numerous articles in recent Annual Reports of the Radiological and Environmental Research Division of ANL).

A data catalogue for the 1975 and 1976 Sangamon experiments is near completion. Hourly observations of the mean wind speeds, wind directions and mean temperaures at 30, 50, 75 and 100 m, and then at every 50 m up to 2000 m above the surface are tabulated. Simultaneous observations of these variables profiled by a tethered kite balloon as high as 250 m above the surface were obtained during the 1976 experiment. Surface geostrophic winds computed from the surface pressure measurements at the microbarograph network installed as part of these studies are also included. In addition, surface-layer observations, including direct solar radiation, net radiation, surface heat flux, friction velocity, mean wind speed and direction, and surface temperature, are given in the report.

Two major MAP3S field experiments addressing PBL pollutant behavior were conducted during 1977. Coinciding with the August 1977 SURE intensive, MAP3S experimenters participated in the Diagnostic Atmospheric Cross-Section Experiment (DACSE-1) that investigated the meteorological and air-quality structure along a vertical cross-section oriented in a WSW-ENE line between Salem, IL and New York, NY, during the period 1-10 August. Data were derived from five soundings per day (the two regular soundings plus three extra soundings taken especially for this experiment) from each of three NWS rawinsonde stations oriented along the Ohio River Valley, vertical profiles obtained by use of aircraft, and from acoustic sounder records. In accord with the conceptual picture of PBL behavior described above, indications were found of regional transport of polluted layers along isentropic surfaces, with little dilution when the layers were isolated from surface processes. Figure 7.1, (Sisterson and Shannon, 1979) is an example of the isopleth analyses of small particle scattering (b-scat) observations made using a nephelometer aboard the PNL DC-3 aircraft. Figure 7.2 illustrates the pollutant profiles from which such isopleths are derived. Corresponding meteorological analyses have been constructed by Sisterson (1979).

The second major MAP3S experiment in 1977 was the Atmospheric Mass Balance of Industrially Emitted and Natural Sulfur (AMBIENS). The intent of this field program was to carry out an integral experiment that inter-related the transport, transformation and deposition processes. Further descriptions of this experiment, emphasizing pollutant transformation and surface deposition, are included in Chapters 8.5 and
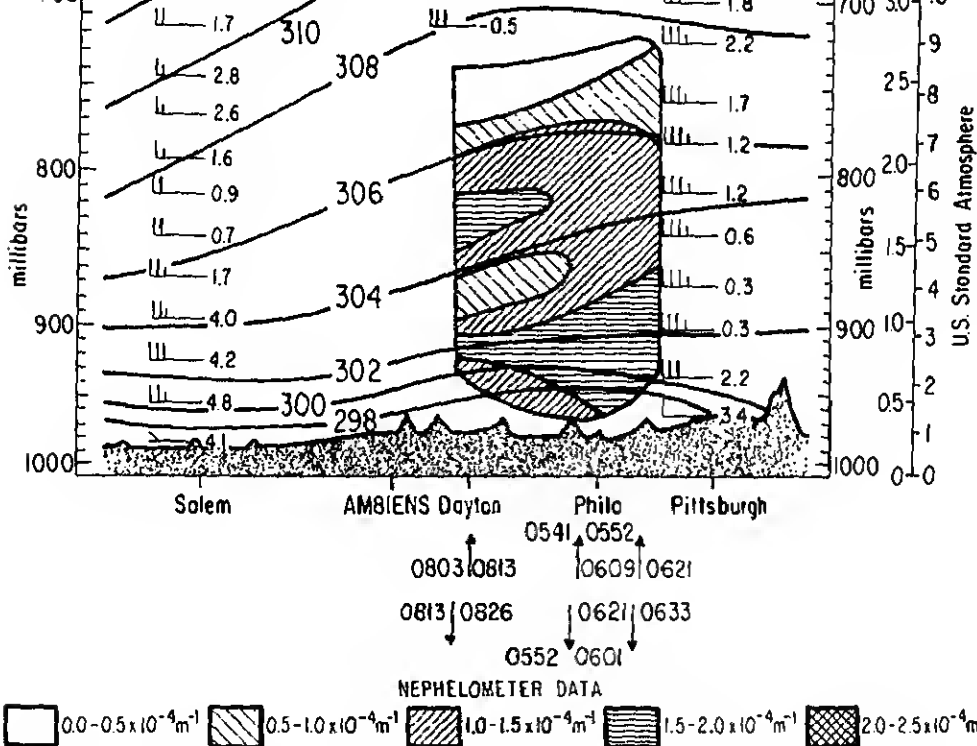
FIGURE 7.1 b_{scat} analysis on August 5, 1977 at 1200 GMT (0700 EST): data from DACSE-I.

layer heights were determined using three different approaches: acoustic sounding (sodar), lidar, and radiosonde temperature profiles. All three methods showed excellent agreement.

Figure 7.3 illustrates the variation of the mixing layer height with time detected by sodar during several days of the AMBIENS experiment. Figure 7.3a contains the cases in which the height increased rapidly with time and soon exceeded the detectable limit (approximately 1 km). Figure 7.3b, on the other hand, shows those cases in which the height never rose beyond 1 km, indicating a rather limited vertical extent for the dispersal of pollutants. Comparison of the two figures and the associated temperature profiles indicates the existence of an elevated inversion, whose altitude was not exceeded by the mixing layer. That is, once the mixing layer developed to the elevated inversion the forcing from below was not great enough to "punch through" to greater heights.
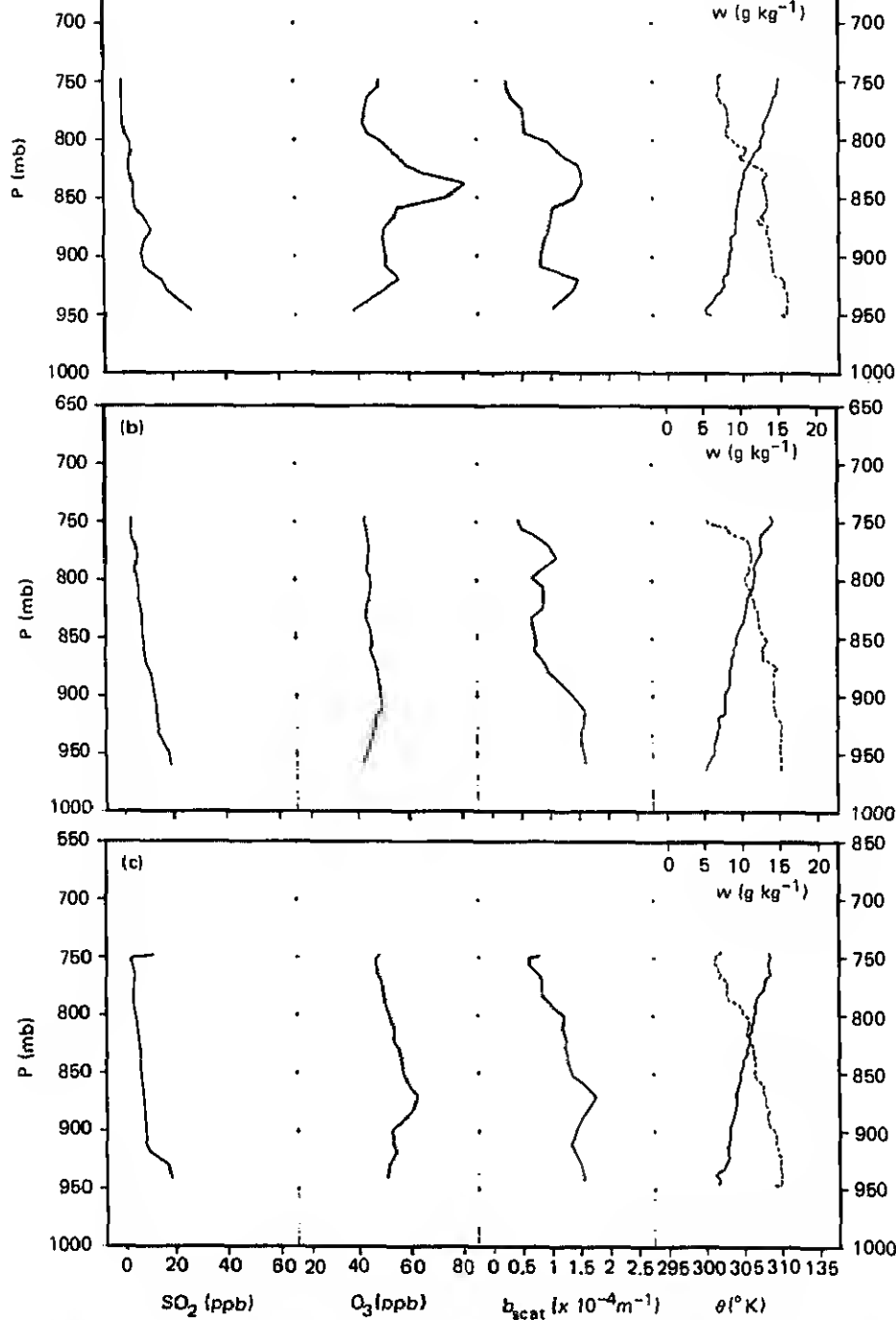
FIGURE 7.2 Profiles of SO_2, O_3, b_{scat}, θ, and w for 1000 GMT …
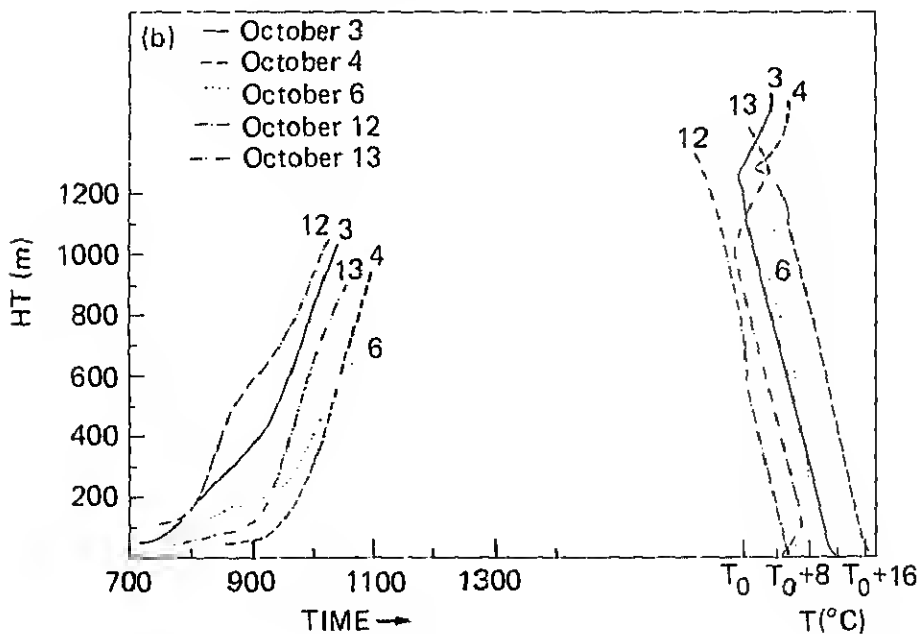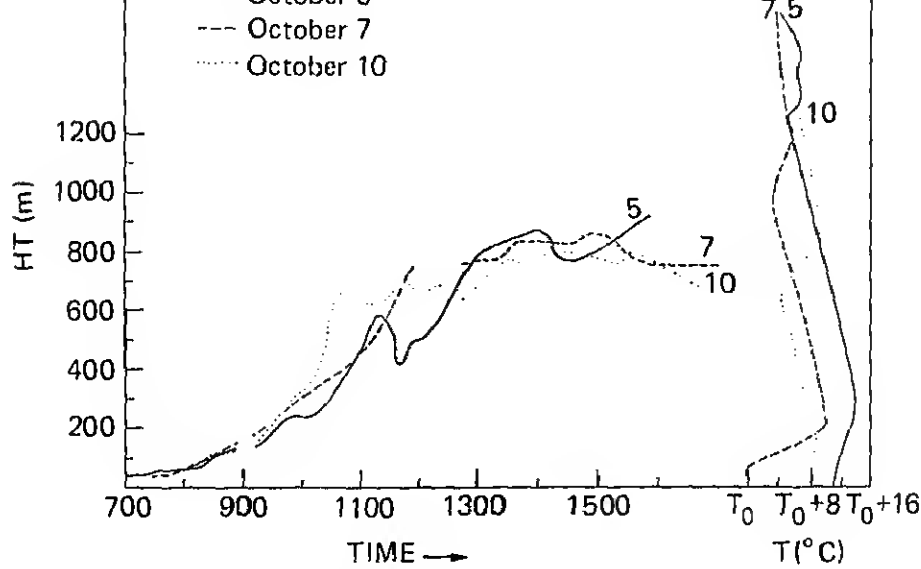
FIGURE 7.3 Variation of mixing layer height with time detected by ANL sodar at Manilla, IN during October 1977. Top shows slowly rising cases, bottom shows rapidly developing cases. Temperature profiles (relative) at the right were taken

difference across the inversion) apparently dictated the length of time it took for surface heating to erode the inversion. A more detailed discussion of these results can be found in Coulter (1977).

The second approach to measuring the extent of vertical mixing relied on use of SRI International's Mark IX mobile lidar system. The vertical aerosol structure was sampled at a rate of approximately three profiles each minute to provide time resolution similar to data being collected by the acoustic sounder unit operated at the site. Each backscatter signature was digitized in real-time with an interval of 5×10^{-8} sec (range resolution of 7.5 m) from the surface to a height of 3.6 km. The lidar system minicomputer was used to generate a real-time, intensity-modulated TV presentation depicting height/time aerosol structure observed over the experimental site, as shown by the example in Fig. 7.4. Picture brightness of the TV display is proportional to the logarithm of observed backscatter. Gradients in backscatter can be used to estimate mixing depth (Uthe and Endlich, 1979).

A comparison of the mixing height as determined by sodar, lidar, and temperature profile is shown in Fig. 7.5. The agreement is seen to be quite good, with the lidar values slightly higher than the sodar, and the temperature profile values slightly lower. In most cases, the differences are less than 75 meters, which is reasonable, for the three methods are sensitive to different atmospheric variables (Coulter, 1977).

7.1.2 Prediction of Day-Time Mixing

The depth to which the day-time mixed layer grows is a function of factors such as the amount of heat flux into the PBL, as well as of the strength of the elevated inversion. Under convective conditions (turbulence due to thermal forcing is much greater than that due to wind shear), the surface heat flux can be related to C_T^2, the temperature structure parameter and to z, the height above the surface at which one measures C_T^2 (Obukhov, 1960, Wyngaard et al., 1971). Sodar data gathered during AMBIENS indicated that the relationship between C_T^2 and z was quite often of the correct nature for the evaluation of surface heat flux via this relationship (Coulter, 1977). Therefore, during the spring of 1978, one of the Argonne sodars was calibrated so that the amplitude of the acoustic signal return could be related directly to C_T^2. A field test of the method was conducted at ANL in June 1978. Measurements of C_T^2 were made using sodar, a laser anemometer, and eddy correlation methods already well established.

The results indicate that remote methods can indeed give reasonable estimates of surface heat flux, particularly from 1000 to 1500 hours LST.
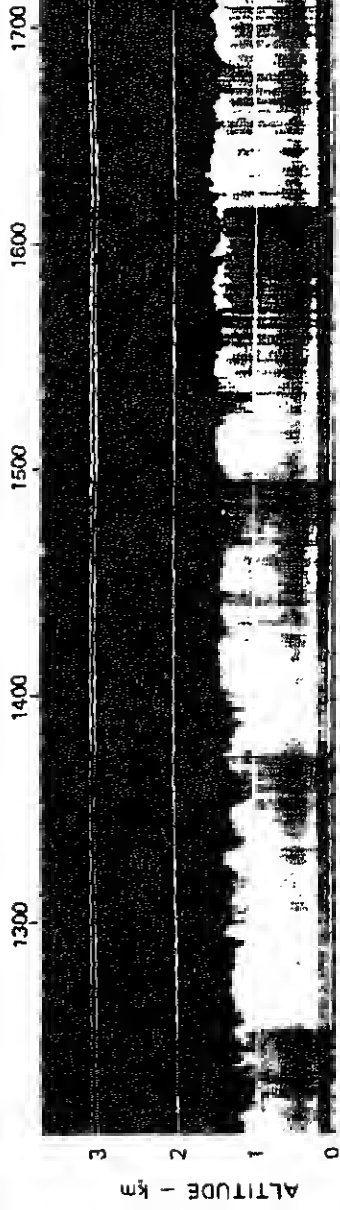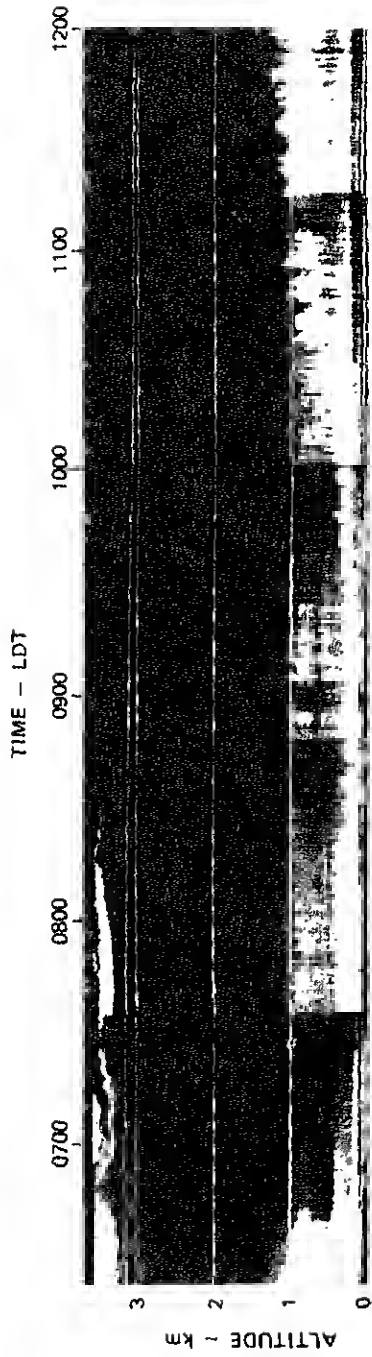
FIGURE 7.4 Lidar-observed aerosol structure over the AMBIENS field site — October 6, 1977. The white line above 3 km is a data plot of the near surface aerosol content as measured by an integrated nephelometer.
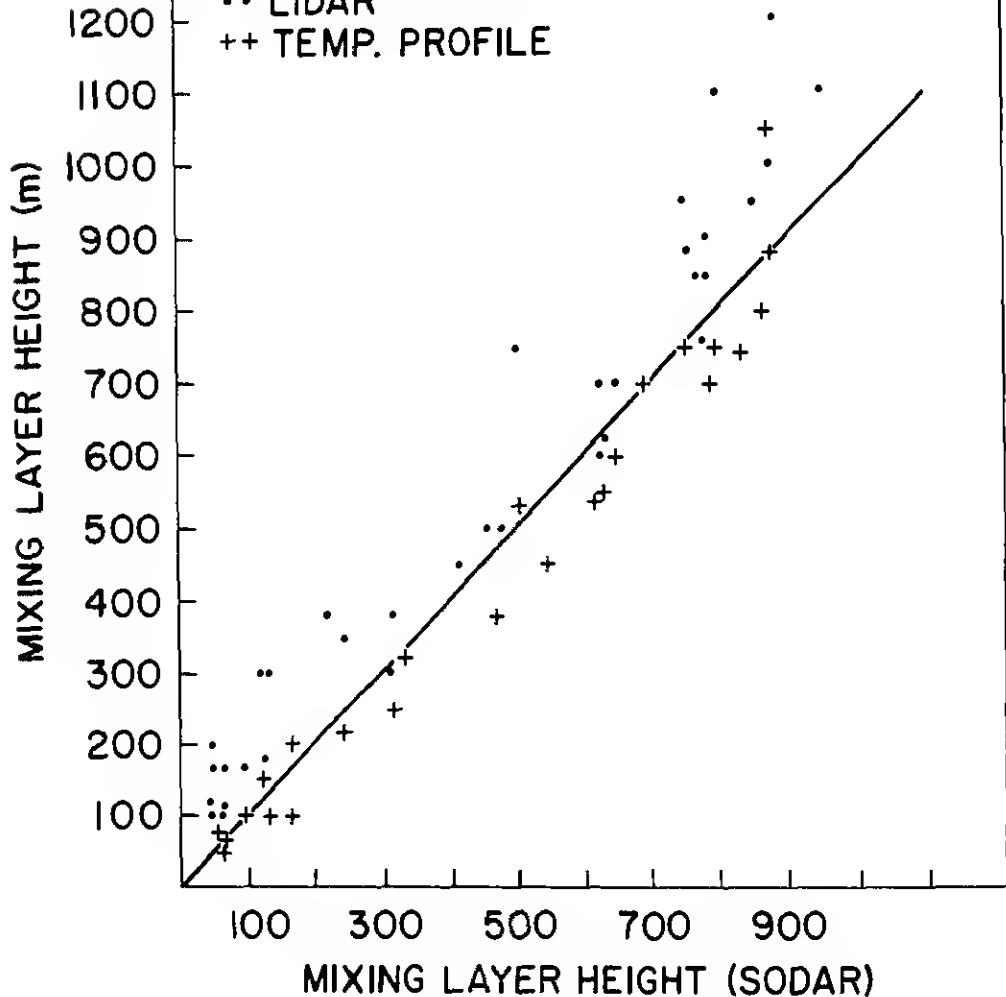
FIGURE 7.5 Comparison of mixing layer heights as determined from lidar and temperature profiles with those derived from sodar returns.

measurements were made. The absolute magnitudes agree very well with one another, usually falling within ± 20%, while the trends agree remarkably well. The variation in heat flux is almost over a full order of magnitude and the rapid decrease is tracked very well. Figure 7.7 is a scatter diagram comparing the three methods over the full experimental period. Both remote sensing methods are plotted versus the eddy correlation method. Some amount of scatter is to be expected due to the
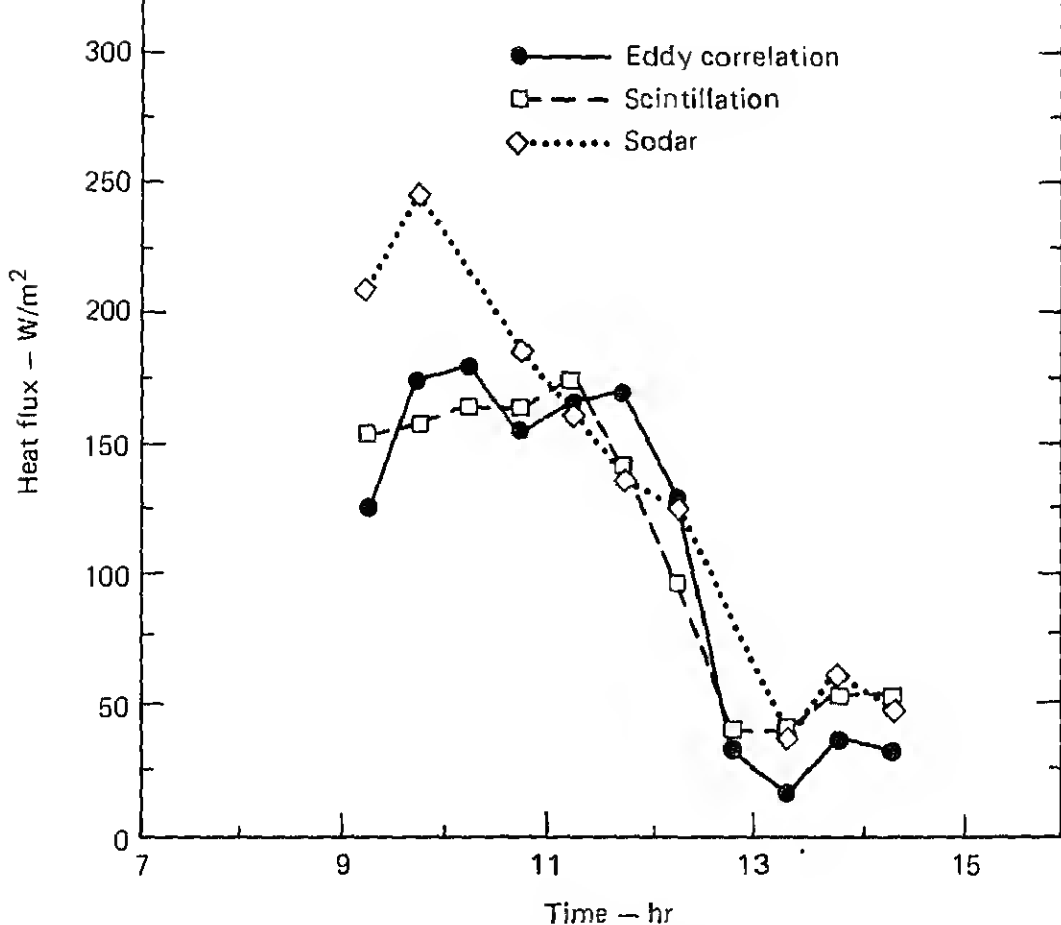
FIGURE 7.6 Heat flux (W m^{-2}) versus time (hr) for three methods of measurement on June 14, 1978 at Argonne.

reasonably good. Almost all the points that are significantly high from the sodar measurements occur during the early morning hours, before 1030 LST, indicating that there may be an additional mechanism at work in the higher elevations (50 meters and above) to which the sodar is sensitive.

For purposes of predicting daytime mixing layer heights, a mixed-layer model with penetrative convection has been tested (Yamada and Berman, 1979) by use of data obtained from two extensive boundary-layer field programs: Wangara, and the 1975 Sagamon experiments. For better prediction it is found to be important to utilize
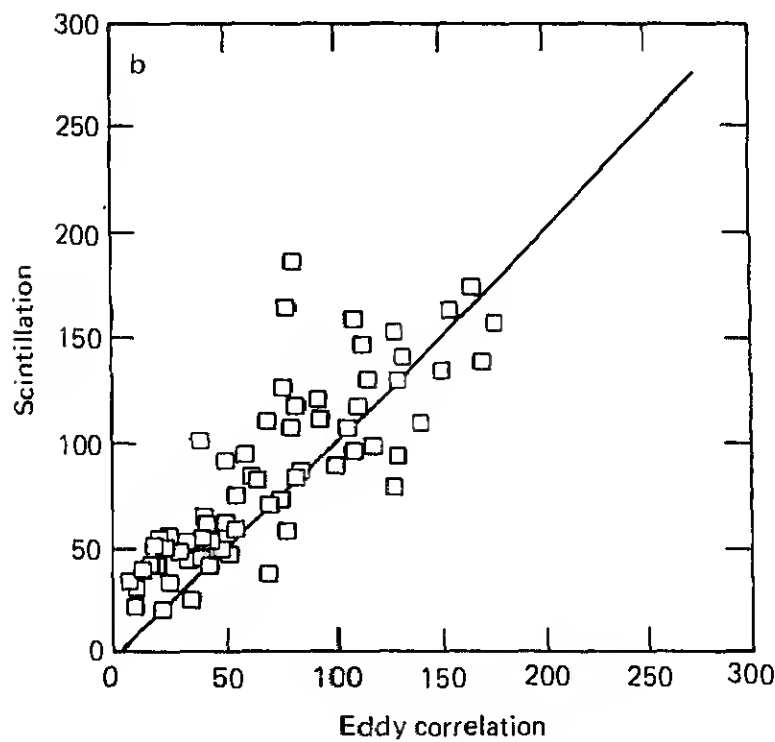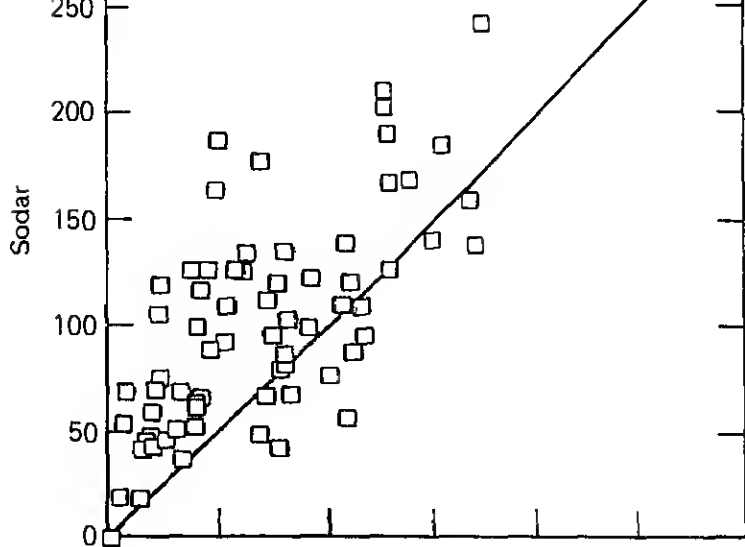
FIGURE 7.7 Comparison of sodar (a) and scintillation (b) derived s

heights are obtained by solving a cubic polynomial equation that is derived from but much simpler than the more familiar differential equations. Inputs necessary to the model are a morning sounding, from which initial mixed-layer height and inversion strengths are determined, and the temporal variation of the surface heat flux. Mixed-layer heights and the surface temperature predicted by the model are compared with observations in Fig. 7.8.
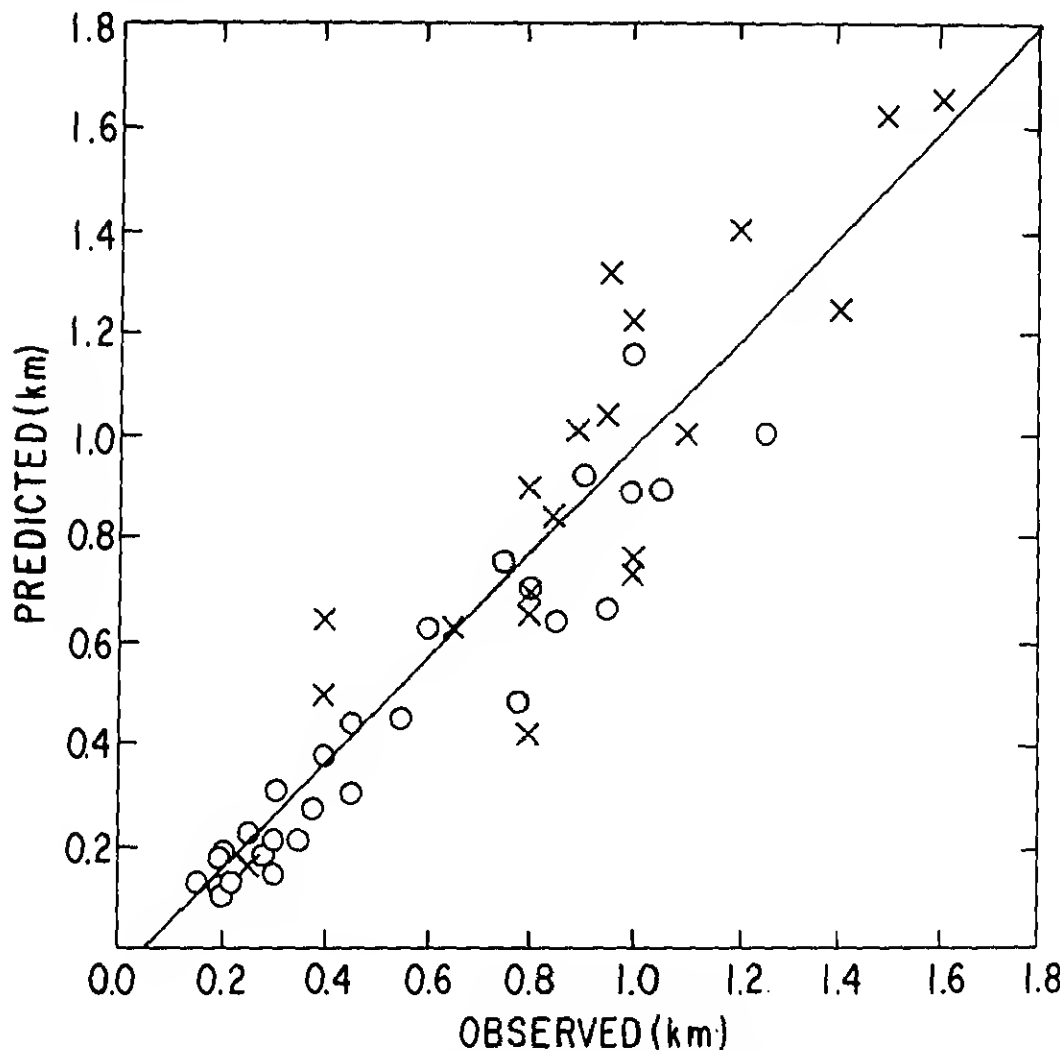
FIGURE 7.8 Predicted and observed mixed-layer heights with C = 0.2 for the Wangara (x) and the 1975 Sangamon (o) experiments.

nocturnal inversion, eddy diffusivities are small and vertical mixing is inhibited. As surface heating progresses a well-mixed layer forms at the ground, working its way upward. By mid-afternoon this mixed layer may extend to a height of few kilometers. Subsequent cooling of the ground in the early evening re-forms the surface inversion and turbulent mixing is once again reduced. Since regional-scale pollutant transport is very much subject to the effects of vertical turbulent mixing in the lower atmosphere, the inclusion of its evolution is of practical importance.

A recent paper by Yu (1978) examined existing diagnostic (Clarke, 1970; Deardorff, 1972; Businger and Arya, 1974), and prognostic (Deardorff, 1971; Zilitinkevich and Monin, 1974) equations used for prediction of the nocturnal surface inversion height, defined as the lowest height where the temperature lapse rate changes to the dry adiabatic. Although the findings are not conclusive, the tested diagnostic equations yield satisfactory results only when the atmospheric stability was either very weak or very strong.

As part of the MAP3S program, a simple prognostic equation for predicting the development of the nocturnal surface inversion height has been constructed from the thermal energy equation (see · Yamada, 1979b). A significant improvement of the present model over previous simple models is the inclusion of atmospheric cooling due to longwave radiation. Another important difference, which considerably simplifies the present model, is the adoption of an empirical expression for the potential temperature profile. Inputs necessary to the model computation are the initial surface inversion height, temporal variation of the surface temperature and an approximate value for the surface heat flux (a value of $-0.008^\circ C$ m s^{-1} has been used in preliminary studies). Surface inversion heights predicted by the present model have been compared with the data of Clarke et al. (1971). A scatter diagram of the predicted and observed surface inversion heights is given in Fig. 7.9. In general, agreement between predictions and observations is good: differences are usually within 50 m.

7.2 TRACERS FOR ATMOSPHERIC TRANSPORT STUDIES

A variety of atmospheric transport and dispersion models are being used in MAP3S and other studies to simulate the behavior of air pollutants and estimate regional concentrations under various scenarios. Attempts to verify the model calculations are complicated by the presence of multiple sources, imprecise knowledge of emission amounts, chemical transformations, dry deposition and precipitation scavenging.
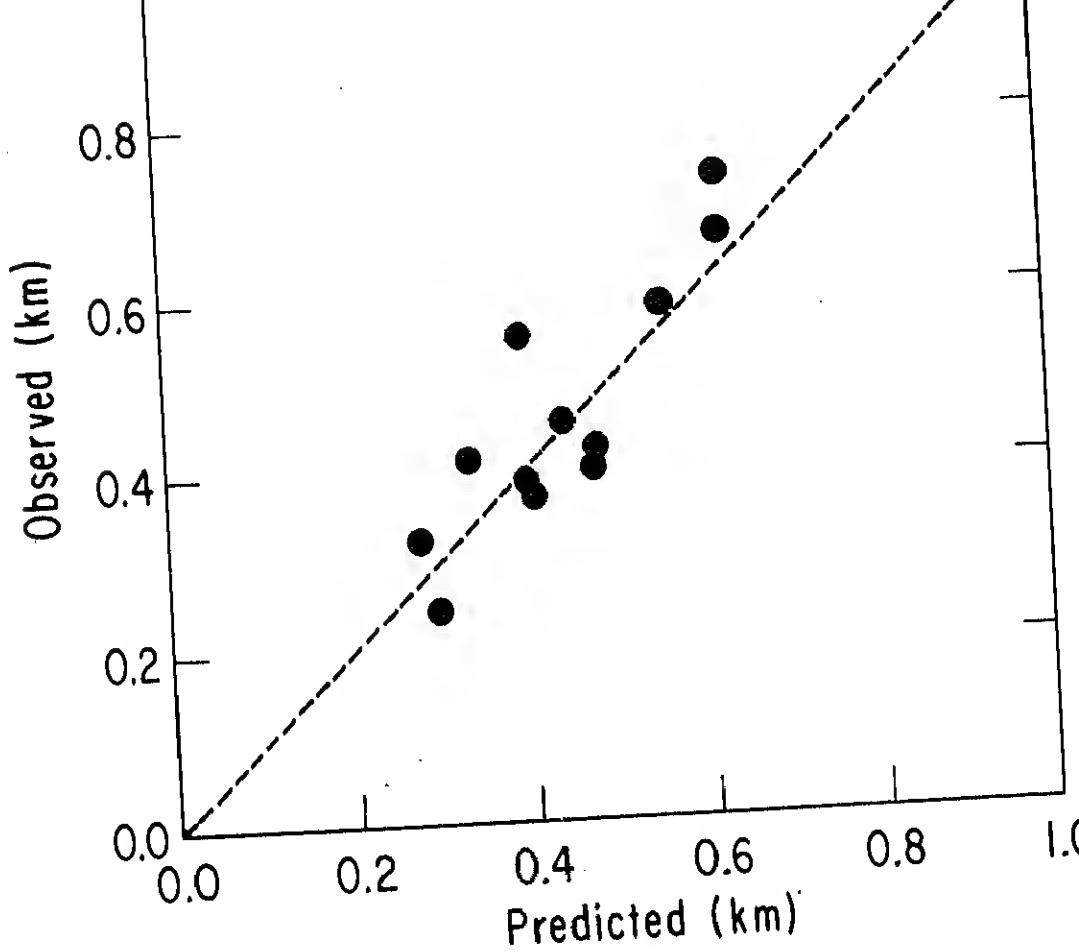
FIGURE 7.9 Comparison of the observed and predicted nocturnal surface inversion heights.

tracers that could be released at a precisely controlled rate an measured accurately at very low concentrations. This will allow us t conduct tracer experiments that isolate atmospheric transport an dispersion from the other complexities and provide data for verificatio of this basic aspect of all model calculations. These conservative trace could also be introduced into pollutant plumes, and transformation an deposition rates could be determined from pollutant/tracer ratios.

A program of regional-scale model verification experiments requir

system is needed with a capability for automated sequential sampling and rapid, reliable sample processing and analysis.

Investigations by J. E. Lovelock, in England, indicated that a perfluorocarbon tracer system could be developed that would be ideal for long-range dispersion studies. The perfluorocarbons are extremely stable, non-toxic compounds, measurable at very low concentrations by electron-capture gas chromatography. Atmospheric background concentrations are well below that of SF_6. Under contract to NOAA/ARL,[*] Lovelock developed three different prototype perfluorocarbon samplers.

The first sampler consists of a pump and a cassette of 24 sampling tubes containing molecular sieve material to trap the tracer. Air is pumped through each sampling tube in a pre-set automated sequence. The cassette is returned to the laboratory and inserted into an analyzer unit that automatically heats each sampling tube in turn to desorb the sample into a catalytic reactor that destroys unwanted components. The sample then flows through a chromatograph column that separates the perfluorocarbon tracer from other surviving compounds and finally passes through an electron-capture detector.

The second instrument combines the sampling and analysis functions into a single unit. The unit contains two sampling tubes so that one is sampling while the other is being analyzed. This "two-trap" instrument provides readout of concentrations every 5 minutes at the sampling site.

The third instrument was designed to be flown in a small aircraft. Ambient air flows through a catalytic reactor that chemically reduces the O_2 and other electron-absorbers, leaving the perfluorocarbon and nitrogen. This is passed directly to an electron-capture detector (no chromatograph column) providing continuous concentration readout with a 3-second delay.

Five cassette samplers, a lab analyzer, and one each of the other prototype instruments were delivered by Lovelock in June 1976. Since then NOAA/ARL has been working closely with EML and BNL in a cooperative effort to develop a practical perfluorocarbon tracer system.

Comparative data on SF_6 and perfluorocarbons (PDCH, PMCH and PDCB) are shown in Table 7.1. The atmospheric background concentration of PDCH is about 0.02 parts per trillion by volume (2 x 10^{-14}), about 1/25 of the SF_6 background. Background of the other two perfluorocarbons (PMCH and PDCB) is another order of magnitude

Tracer	Sulfur-Hexa-fluoride	Perfluoro-dimethyl-cyclohexane (PDCH)	Perfluoro-methyl-cyclohexane (PMCH)	Perfluoro-dimethyl-cyclobutane (PDCB)
Formula	SF_6	C_8F_{16}	C_7F_{14}	C_6F_{12}
Mol. Wt.	146	400	350	300
Background (pptv)	0.5	0.02	0.002	0.002
Cost/kg	$7.	$45.	$45.	$45.
Relative Release Rate	100	11	0.9	0.8
Relative Cost/ Release	100	70	6	5

lower. The amount of tracer released in any experiment must be sufficient to distinguish the plume from background at the maximum sampling distance. The required release rate for PDCH is about 10% of that for SF_6; for PMCH and PDCB it is about 1% of the SF_6 rate. Taking the higher price of the perfluorocarbons into account, the PDCH required for an experiment would cost about half as much as SF_6; the cost of PMCH and PDCB would be less than 5% of the SF_6 cost.

7.2.1 Idaho Tracer Experiment

Perfluorocarbon release, sampling, and analysis techniques were successfully tested in a field experiment in Idaho on April 19, 1977. Three perfluorocarbons were released simultaneously with SF_6. Whole-air samples were collected at nearly 100 sampling sites along arcs at about 2-, 50-, and 90-km from the release point. The Lovelock cassettes and "Two-Trap" samplers were operated on the 50-km arc and the continuous sampler was flown along with a new BNL continuous instrument based on the Lovelock design.

The Idaho experiment demonstrated that:

2. The five cassette samplers, set up at 3 km intervals along the 50-km arc, performed well. About 60 half-hour samples were taken and all data are consistent. As shown in Fig. 7.10, as the plume passed the arc, concentrations increased from the background of about .02 ppt to a peak near 10 ppt and down to background again.

3. The "Two-Trap" sampler was operated beside one of the cassette samplers and provided real-time five-minute readings that agree well with the cassette data, as shown in Fig. 7.11. Average concentrations obtained by the two instruments agree within 5%; however, the detection limit of the cassette sampler is two orders of magnitude better than the "Two-Trap" at present.

4. Perfluorocarbon measurements from the sequential samplers agreed well with the SF_6 measurements from whole-air samples taken at the same locations.

5. The airborne real-time continuous sampler required further modification. Subsequently, the BNL version of this instrument has been successfully flown in the AMBIENS experiment (see Sec. 8.5) in October 1977 and for EPA in the STATE experiment in August 1978.

7.2.2 Recent Developments

The Idaho experiment established that the sequential samplers worked well and that PDCH can be measured reliably down to its background level of about .02 ppt. However, the molecular sieve traps used in these instruments do not collect PDCB or PMCH, both of which have background concentrations about 1/10 that of PDCH. In exploring perfluorocarbon trapping and analysis techniques at BNL, Dietz has found that charcoal efficiently traps all three tracers but also collects many unwanted components that interfere with perfluorocarbon analysis. A laboratory analysis scheme has now been devised that effectively eliminates interferences and achieves a sensitivity better than .001 ppt (1×10^{-15}). This achievement has led to a new concept for a sequential sampler using charcoal traps, that would be light-weight (about 12 lbs.), powered by self-contained batteries, and smaller, simpler to operate, and less expensive than the Lovelock samplers. The sampler would automatically start at a preselected time and take a preset number of samples (up to 24) of preselected duration (up to 24 hours per sample). The concept appears so promising that plans to build a quantity of Lovelock samplers have been postponed until a prototype of the new
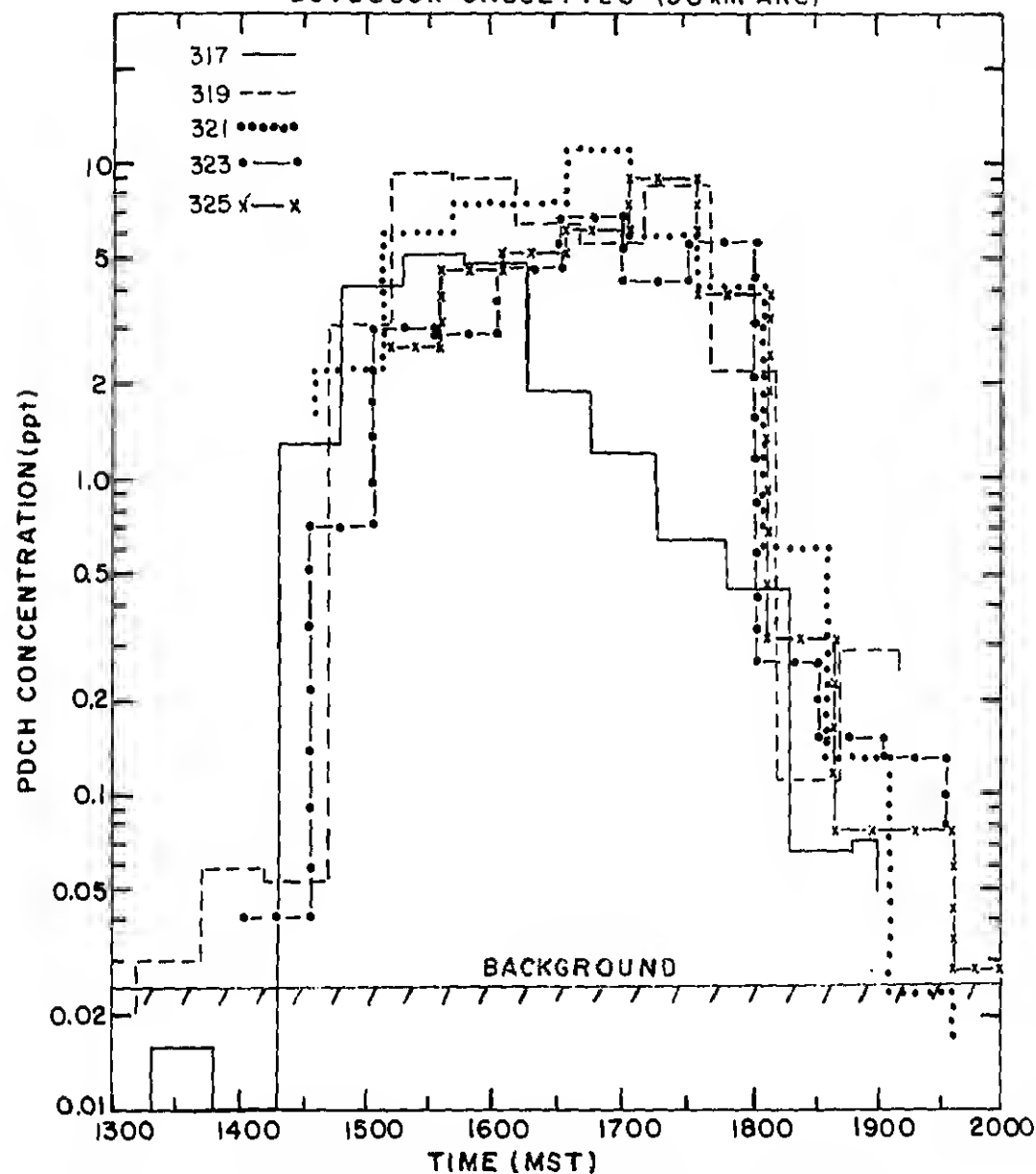
FIGURE 7.10   PDCH concentrations in 1/2-hour sequential samples at 5 locations (317-325) in the 55 km arc.
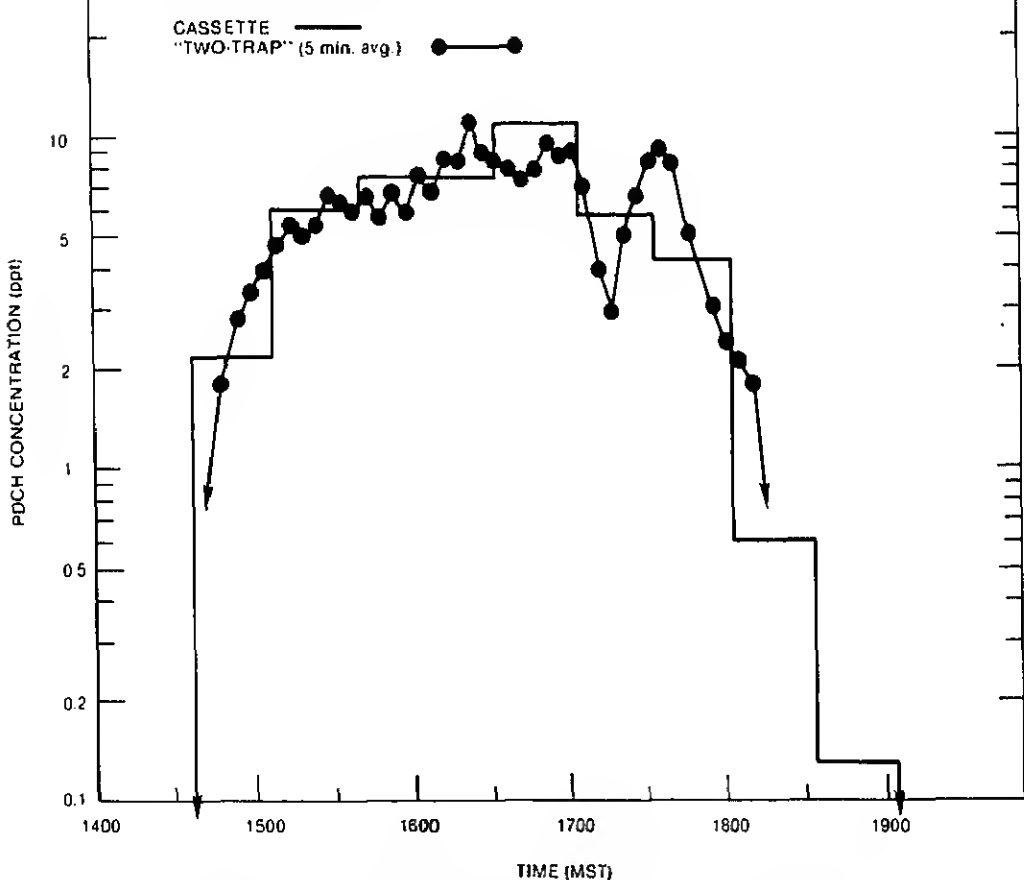
FIGURE 7.11 Intercomparison of "two-trap" and cassette sequential sampling data at site 321.

February 1979. Tests shold be completed by May and, if successful, NOAA/ARL plans to contract for production of about 60 units to be delivered within 6-9 months (i.e., winter of 1979-80). It is also planned to modify the existing Lovelock samplers for use with charcoal traps.

For the future, the use of capillary chromatography is under study as a means of achieving greater separation of tracer from interfering compounds. This technique has the potential to increase our measurement capability from the present parts in 10^{16} range to parts in 10^{18}. Other fluorinated compounds with sufficiently low atmospheric background concentrations are being sought to enable us to take advantage of this capability.

Major effort within MAP3S is being devoted to the representation of transport processes in numerical models. On the local scale it is often satisfactory to use a single nearby wind to represent horizontal transport, or to choose a single depth of the atmosphere through which to let pollutants mix. On the regional scale, however, spatial and temporal inhomogeneities must be considered for there to be any hope of representing pollutant dispersion.

Developing the capability for gathering and processing the data to generate such information for use in air quality models had received rather limited attention prior to MAP3S. Heffter et al. (1975) developed a trajectory model that used the routine rawinsonde data taken every twelve hours to generate a horizontal wind field. Wendell et al. (1976) also developed a similar formulation and similar approaches have been used by European researchers, except that they often have data available at six hour intervals.

The approach used by these groups has been to interpolate available data in space and time in order to develop the trajectory information, often at hourly or three hourly intervals and with spatial resolution of 50 to 100 km. This approach has been used in virtually all of the regional models, including those of Heffter et al. (1975), Wendell et al. (1976), Sheih (1977), and Meyers et al. (1979). Results from some of these models are described in Chapter 12.

When applied to the Eastern United States, however, this approach results in a number of problems and simplifications that may be drastically affecting the results. Among these limitations are the following:

- There are only about 20 rawinsonde sites in the region; therefore, spatial resolution of the data is not as fine as for data on topography, emissions, surface type, etc. Further, frontal systems are poorly resolved, making it hard to determine back trajectories of air parcels undergoing precipitation scavenging.

- The two observations each day are taken near sunrise and sunset (0700, 1900 EST) and are thus unable to indicate directly either the height to which pollutants mix during mid-day or the intensity of the frequent nocturnal inversions. Interpolation between the two data times may thus be quite inaccurate, particularly for the planetary boundary layer.

- Interpolation, as it is now done, takes incomplete account of topography. Although the observations implicitl

convention is to assume that air flow moves in layers of constant thickness above the terrain (i.e., two-dimensional flow, no vertical velocities), thus obviating any representation of channeling of air up the Ohio River basin, around the Appalachians, down the Hudson River Valley, etc.

Because of these and other difficulties, a new approach was deemed necessary. Two choices appeared possible.:

- Develop a new interpolation and analysis method that imposes appropriate diagnostic constraints on the interpolation process while at the same time developing the capability for including additional data (e.g., hourly surface winds and temperatures) as methods for reducing problems of rawinsonde data limitations.

- Develop and utilize prognostic (i.e., dynamic) numerical models that actually calculate the wind, temperature, and precipitation fields based on appropriate physical laws given initial conditions.

There are of course advantages and disadvantages to each approach. The first, while more complex than the present interpolation process, is considerably less demanding than the second approach. The second approach, however, ensures satisfaction of dynamic constraints while the first only meets the constraints in a diagnostic sense.

In MAP3S, both approaches are being pursued. The first, described in the rest of this section, is viewed as being achievable within a few years while the second, described in Chapter 7.4, will take considerably more effort and research. Further this latter approach will likely be used only for special case studies rather than for long-term assessments.

7.3.2 BNLMET Model

7.3.2.1 Introduction

A diagnostic meteorological model has been developed that can develop physically consistent meteorological fields from various types of incomplete meteorological data that are available at random places in space and time, including the effects of complex terrain. This model, named BNLMET, uses the method of calculus of variations, employing conservation of mass and total energy constraints, to adjust objectively analyzed and observed meteorological data. Implementation of an additional constraint based on conservation of momentum has been recently tested, but is not yet incorporated. This work is based on earlier development in cooperation with William Ohmstede of White

constraints, resulting in velocity, temperature, humidity, and pressure fields over the region. Typically the analysis goes from the ground to the tropopause, and accounts for the effects of complex terrain.

Probably the single most important advance needed to improve the accuracy of simulations with atmospheric transport models is improvement in specifying the three-dimensional structure of the transport field. The accuracy and utility of air quality modeling codes must ultimately, in the limit of accurate numerical methods, depend upon knowledge of winds, turbulence and, in general, the different properties of the atmosphere. Yet, objectively incorporating realistic temperature, humidity, mixing depth, and terrain influences into regional transport models is difficult.

In the past, without the types of analyses available from BNLMET, it has been virtually impossible to incorporate consistent physics because of errors in the data. Two types of errors are always present in the data, due either to instrumental inadequacies or the fact that measurements incorporate instantaneous effects of turbulence rather than providing an appropriate mean value. Implementation of BNLMET helps to reduce the effects of these errors by improving the method of interpolation or "nowcasting". This is done by "adjusting" the data according to certain physical constraints. The numerical objective methodology reconstructs the meteorological fields in a way suitable for use in meso/regional scale transport and diffusion models. The approach is intended to properly balance concern for realism within the limitations of computational efficiency and physical understanding. The approach relies heavily upon taking advantage of certain conservative properties of fluids.

Commonly, pollution is confined to distinct layers because of the occurrence of a stable (non-turbulent) layer capping these material layers. The behavior of the atmosphere can be fully understood only if adequate recognition is given to the importance of material layers. The objective of the BNLMET program is to evaluate the atmospheric variables required by application of routines that calculate the transport from prescribed sources within the material layers. Briefly the program performs diagnostic analysis that involves three distinct but related functions:

- Upper air meteorological data are processed to identify material layers having extensive time/space continuity. The first step is single station analysis of each observation to identify possible material layers. Results from single stations are then used to select the appropriate material layers that maintain time/space continuity over the region.

the meteorological variables for each material layer and at each time interval from the processed observations. The OBJANL subroutine uses the methods of Gandin (1964) to provide the optimal interpolation of the meteorological data from a random to a uniform grid. Important scales in OBJANL are the spatial radius of consideration of meteorological data from a point and the characteristic velocity relating the time and space scales. This objective analysis produces the initial quantitative estimate of the meteorological fields.

- Variational analysis of the observed fields is then performed to force compliance with functional constraints that explicitly introduce terrain and adiabatic considerations. The variational analysis makes adjustments and finds meteorological fields that minimize the error between the observations and such physical constraints as conservation of mass, energy and momentum. The variation is performed in space and time.

7.3.2.2 Variational Analysis

It is the variational analysis step that is the crucial element of BNLMET. The independent variables are time (t) and Cartesian space coordinates (x,y,z). The principal dependent variables are the thermodynamic state variable, consisting of pressure, temperature, density, specific humidity, and the kinematic variables consisting of the velocity vector, the momentum (or mass flux) vector, and the water flux vector. The more important turbulence terms are the turbulent heat flux vector, the turbulent mass flux vector, the turbulent water flux vector, the Reynolds stress vector, and the turbulence pressure.

The functional basis for this development is a rather standard system of equations, including the equation of state, the continuity equation, and supporting dynamic equations in a turbulent atmosphere. Since viscous effects are negligible in comparison with turbulence effects, the fluid is presumed to be inviscid. The equations of motion govern the behavior of the momentum. The total energy includes terms representing the rate at which heat is added per unit volume by radiation and by physical and chemical processes (e.g., the rate at which latent heat is added by condensation of water vapor).

A normalized material layer integral operator is defined to help describe the physics within the layer. This results in higher moments of some variables in each of the equations. A property of the equation for any moment is that it couple with the next lower moments. To be solved, the total set of equations that describe the evolution of the moments must be made into a closed system, but from the standpoint of

In each version, Euler-Lagrange equations are derived. Then the variational method is employed, using over-relaxation, to minimize the weighted errors between the objective analysis terms and the terms of the state and dynamic equations.

7.3.2.3 Modeling Results

In this section preliminary illustrative results of meteorological analyses by BNLMET are given for a typical meteorological case, October 2-3, 1974, during which a high pressure system moved in from the Midwest as a weak low pressure center filled and moved northeastward across New England.

The numerical grid is illustrated in Fig. 7.12. The grid has 25 kilometer spacing and the box is 600 kilometers on a side; tick marks are every 100 kilometers. Black dots are upper air sounding sites; there are twelve additional sites used, but these are outside the map shown.

Figure 7.13 shows the terrain height elevations above sea level. This and all other projection views are looking 45° down from southwest to northeast; north is in the upper left corner. Minimum and maximum values are indicated by LOW and HI, respectively.

Figures 7.14 and 7.15 represent results of objective analysis (OBJANL) for October 2, 1974 at 00Z for the transport layer. Figure 7.14 shows the mean layer wind (m s^{-1}); for this and all other wind fields the largest arrow indicates winds of 16 to 20 m s^{-1} and the smallest indicates winds of 1 to 5 m s^{-1}. In the objective analysis, winds and other meteorological variables from outside the grid are used in the interpolation. Input data are primarily at 00Z and 12Z. Only one station reported at 18Z and none at 06Z.

In contrast to the results from the objective analysis (OBJANL), the variational analysis (VARANL) for October 2, 1974 (Fig. 7.16 and 7.17) uses data only from the objective analysis results within the grid. The mixing depth is shown at six hour intervals from October 2-3, 1974 00Z in Figs. 7.17 and 7.18a-d. Comparing these results with evolution of the wind field features shows quite good correlation between the two fields (Meyers et al., 1976). The inversion height generally appears smoother, but by no means flat, in comparison to the mixing depth. The sequence illustrates the progressive collapse of the cold air dome from a maximum height of approximately 5360 meters at 00Z on October 2, 1974 to a maximum of 3120 meters at 00Z on October 3, 1974.

7.3.2.4 Discussion
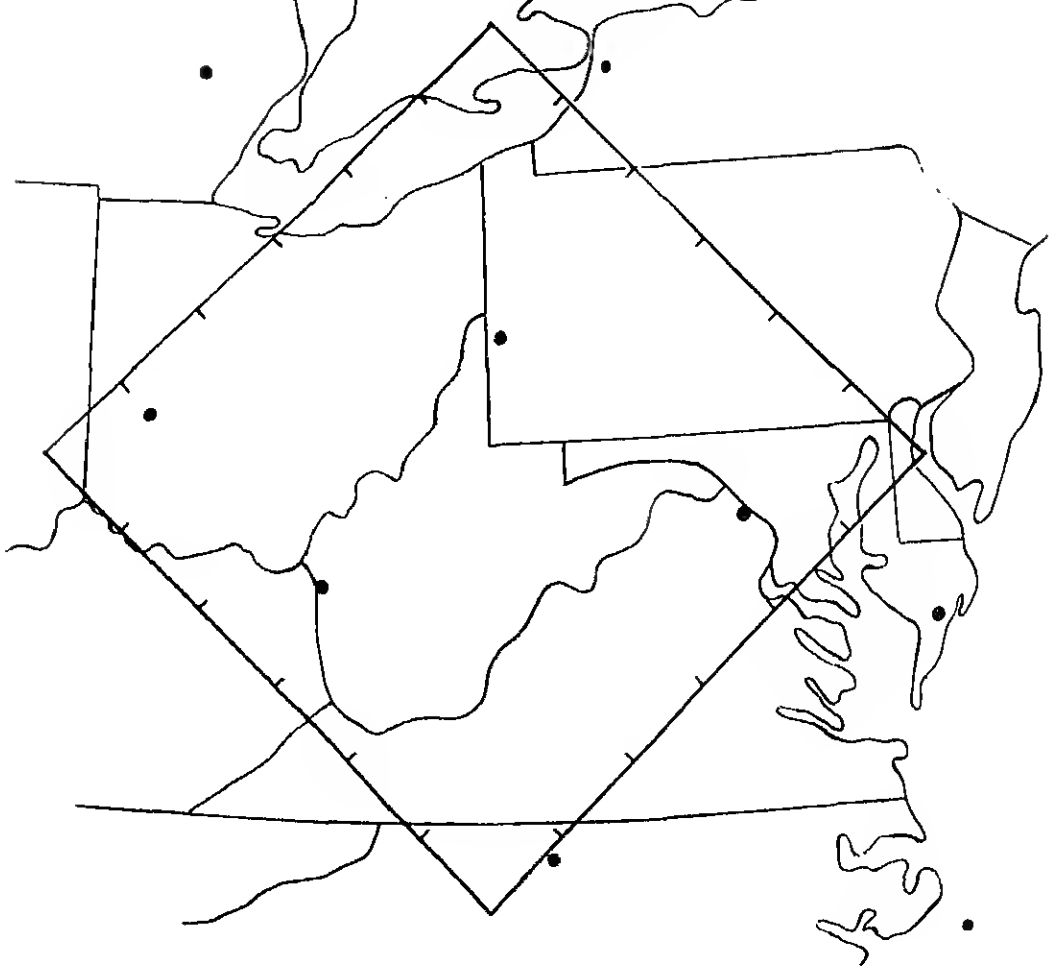
FIGURE 7.12   Location of grid and upper air soundings.

hand, because of the complexity of the meteorological analysis required to objectively interpret the data. For example, a standard objective analysis estimate of the mixing depth of 1 kilometer would provide a dilution of concentration of a vertically well-mixed plume of approximately 1/5 to 1/2 that of the variational analysis for the above case. The corresponding deposition rates would be 2 to 5 times greater than for the variational analysis results.

Both complex and simple air quality model codes can be easily interfaced with the processed meteorological fields from BNLMET. The processing of the analyses takes only a few minutes of CDC 7600
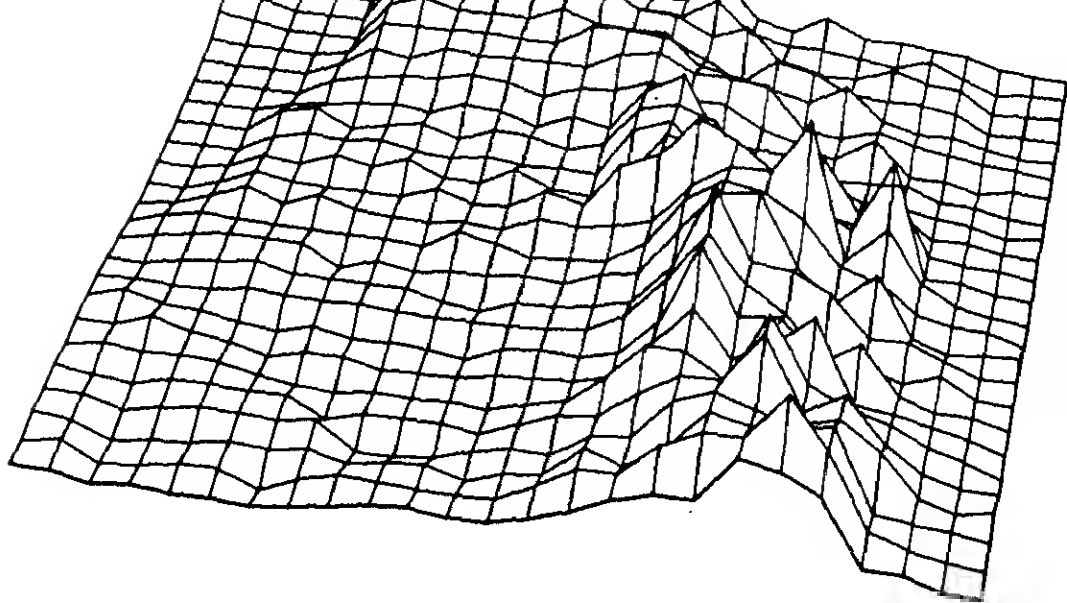
FIGURE 7.13 Terrain surface in grid.

At present a variety of improvements are being considered, including
incorporation of surface measurements as input, more realistic
treatment of fronts in both the objective and variational analyses,
inclusion of momentum constraints (which have been successfully tested)
and addition of more diabatic effects (e.g., surface energy budget
considerations as described in Hoffert and Storch, 1978). These
improvements should increase the robustness and accuracy of the model.

Finally, regional field experiments will be needed to expressly test
the model.

7.4   DYNAMIC REPRESENTATION OF REGIONAL TRANSPORT

As explained earlier in this chapter, reasonably accurate, detailed
knowledge of regional meteorological conditions in three-dimensions and
time is required to simulate long-range pollutant transport.
Unfortunately, as discussed in Sec. 7.3, the distributions of wind and
temperature aloft are measured only twice a day (0000Z and 1200Z) by
the radiosonde network of the National Weather Service, which has an
average grid spacing of about 400 km. Due to the comparatively coarse
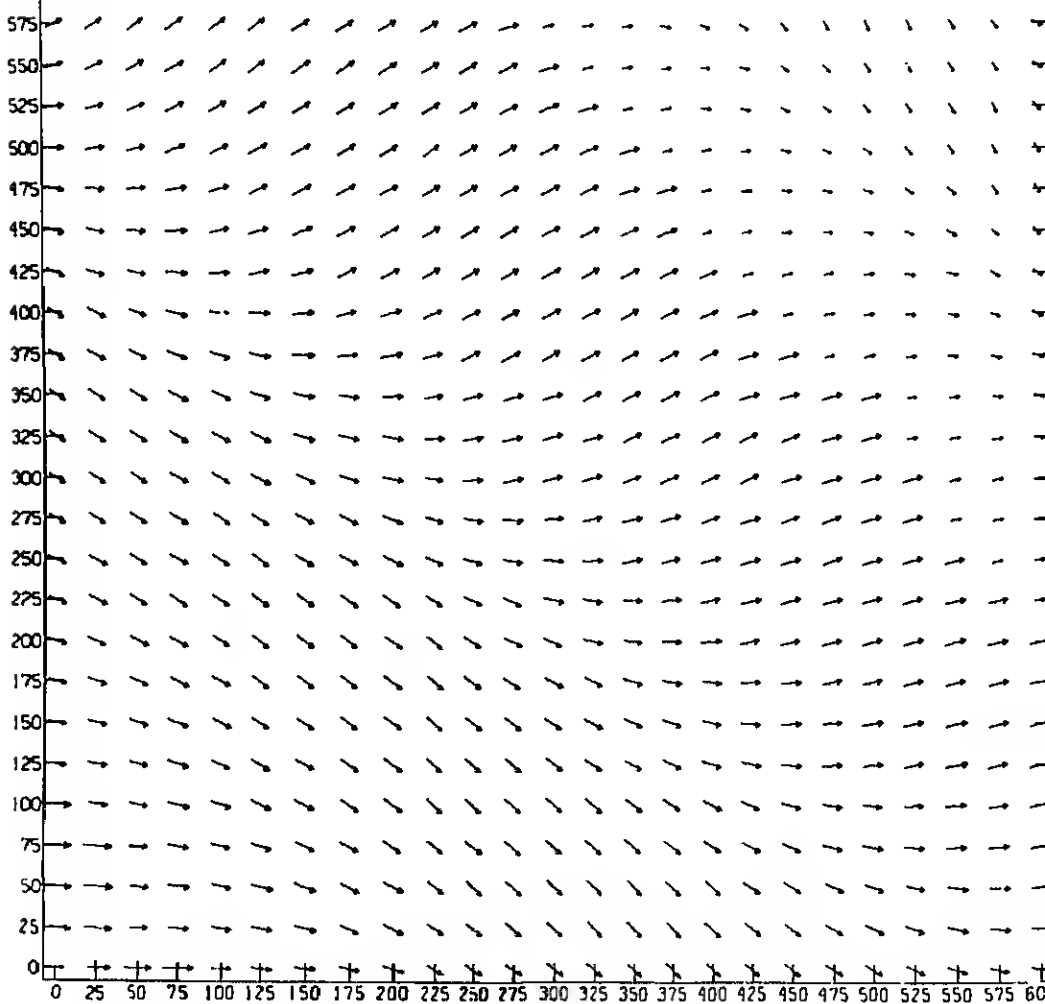
FIGURE 7.14   Mean layer wind, October 2, 1974, 00Z, OBJANL.

insufficiently detailed for consistently accurate predictions of the resultant pollutant concentrations. The most critical deficiencies are caused by the quite coarse vertical resolution (typically 500 m) and the long time interval (12 h) between measurements. In general, pollutants are emitted into the atmosphere either near the surface or, at most, in the lowest few hundred meters of the atmosphere, where the vertical gradients of wind, temperature, and water vapor are largest and the temporal variations are greatest. It follows, therefore that to improve the simulation of regional pollutant transport, improved data coverage in
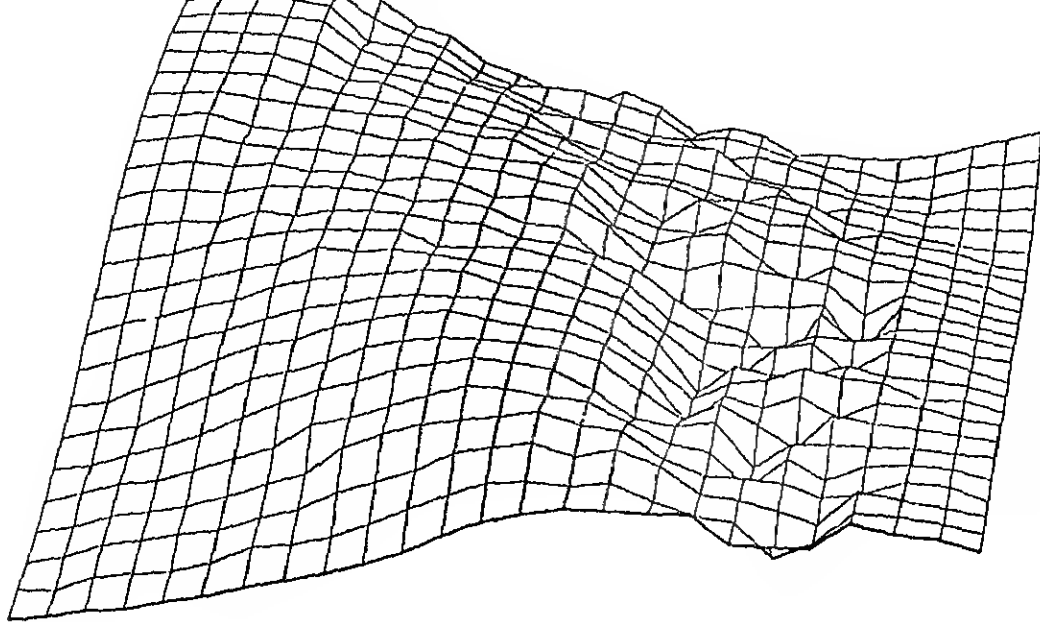
FIGURE 7.15   Mixing depth, October 2, 1974, 00Z, OBJANL.

Section 7.3 described an analysis approach that improves on the traditional interpolation techniques. Another alternative is to generate detailed, regional wind and temperature fields by numerically integrating an appropriate set of dynamic equations. This approach is both costly and complex, but offers the only means for being able to actually predict short-term future conditions and to create more detail than is provided by the observational data. One serious limitation to numerical modeling of these turbulent circulations arises from the fact that the hydrodynamic equations for turbulent flows are not closed. The equations of motion contain unknown second-moment turbulence quantities, the second-moment equations contain unknown third-moment quantities, and so on. The number of unknowns always exceeds the number of equations.

One solution of this dilemma has been to "parameterize" the extra variables in terms of some combination of the known variables. A first-order closure hypothesis of this kind relating the Reynolds stresses to wind gradients was proposed by Boussinesq (1877, according to Schlichting, 1968; p. 544) who introduced the concept of an eddy viscosity coefficient analogous to the coefficient of molecular viscosity
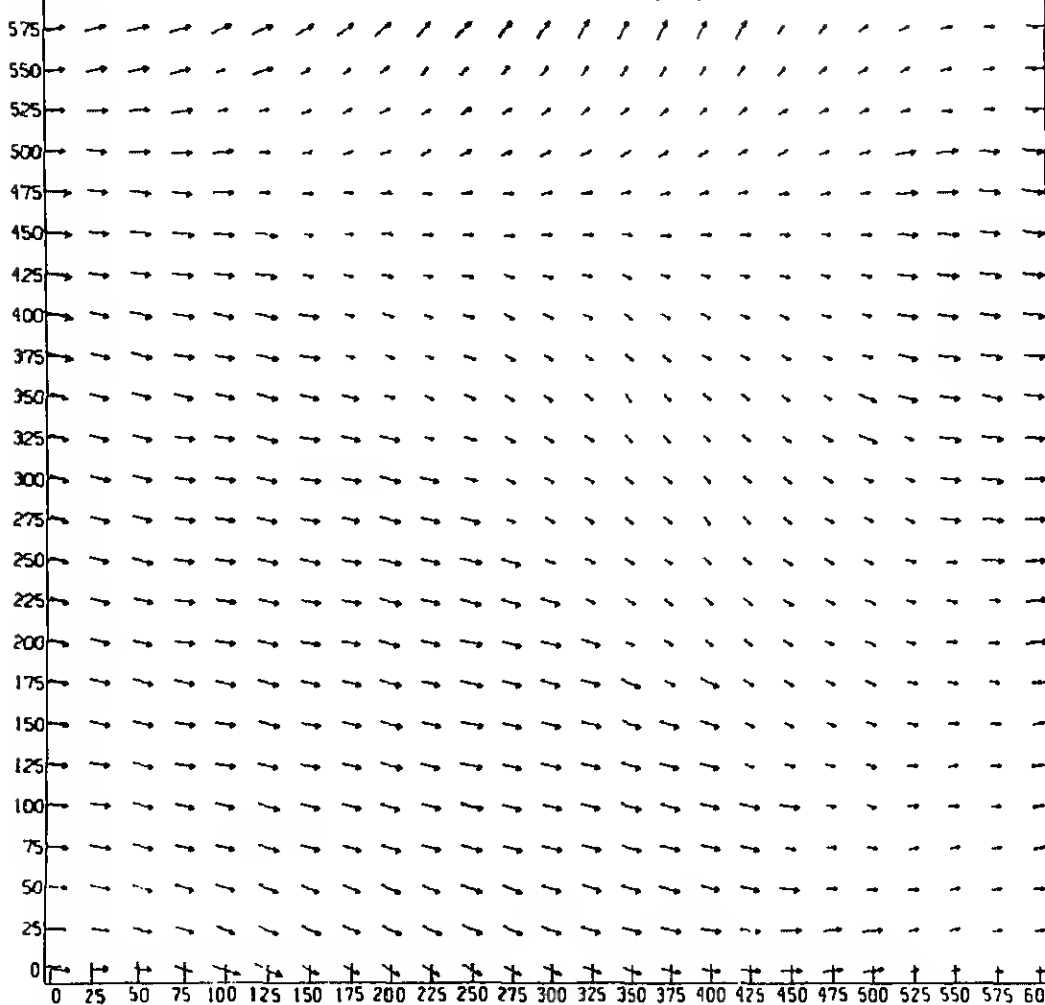
FIGURE 7.16 Mean layer wind, October 2, 1974, 00Z, VARANL.

the flow. Various empirical expressions for the eddy viscosity ranging from a constant value to a simple function of stability have been proposed. For example, in a review paper on the atmospheric boundary layer, Zilitinkevich et al. (1967) presented profiles of the eddy viscosity coefficient obtained at various sites. Magnitudes ranged from 10^{-1} to 10^2 m^{2}s^{-1} and distributions with height varied considerably with type of terrain and time of day. Clearly no simple expressions for an eddy viscosity coefficient can ever be expected to account in detail for the complex variations of turbulent mixing that occur in the real atmosphere.
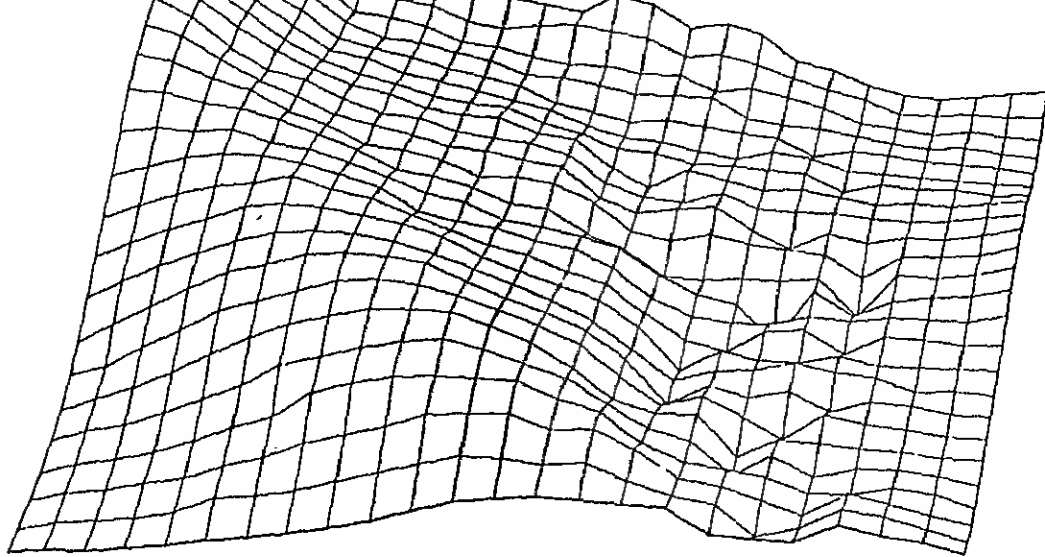
FIGURE 7.17   Mixing depth, October 2, 1974, 00Z, VARANL.

To properly reproduce the wind fields over the MAP3S region, it is necessary to include the topography of the region. Among existing three-dimensional mesoscale numerical models, there are several that include the effects of topography (e.g., Mahrer and Pielke, 1977; Lutz and Kreitzberg, 1977). These models are based on the eddy-viscosity method for parameterizing turbulent fluxes. Another approach is to use second-moment turbulence-closure models (hereafter referred to as closure models) that are based on the second-moment turbulence equations. The latter models seem to be less restrictive than the eddy-viscosity parameterizations.

As part of the MAP3S modeling program we have been considering the use of such models as a means of better defining the state of the atmosphere and defining transport. We expect, however, that these approaches will be most useful mainly for study of very special test cases.

7.4.1. The ANL Turbulence Closure Model
A second-moment turbulence-model developed at Princeton University (Mellor, 1973) has been shown to be capable of simulating various turbulent flows encountered in atmospheric (Yamada and Mellor, 1975) and oceanic (Mellor and Durbin, 1975) boundary layers. Successful use of similar closure models has been reported by others (e.g., Lewellen

(a)

(b)
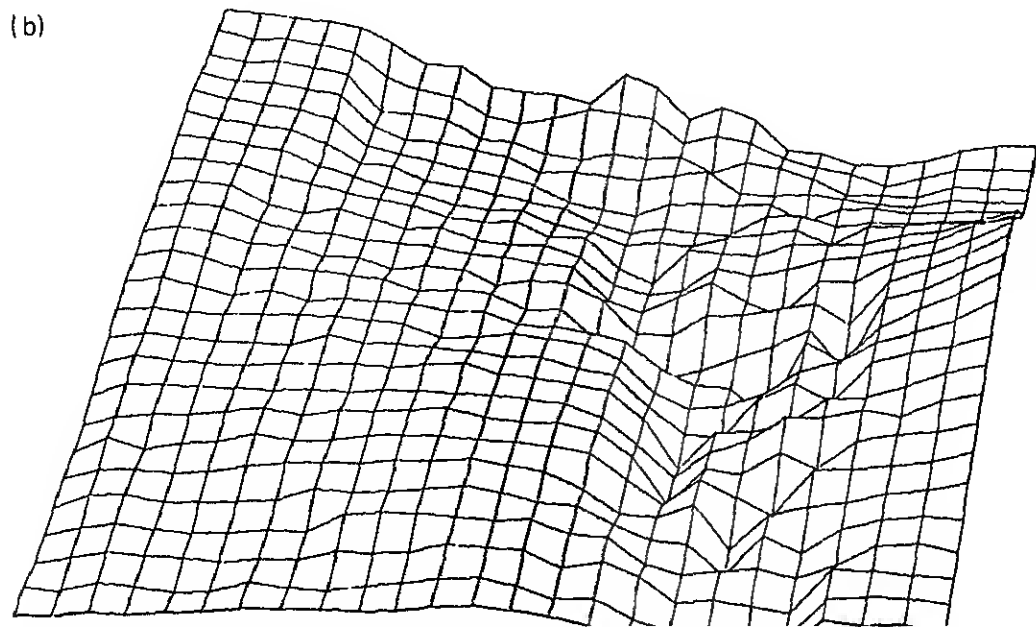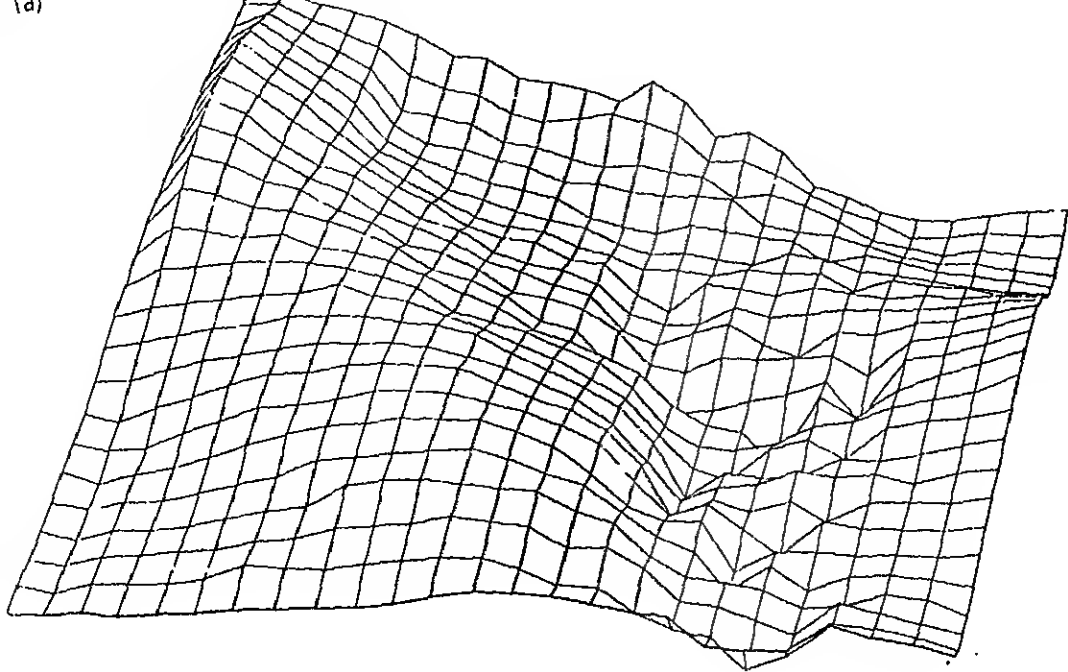
(c)
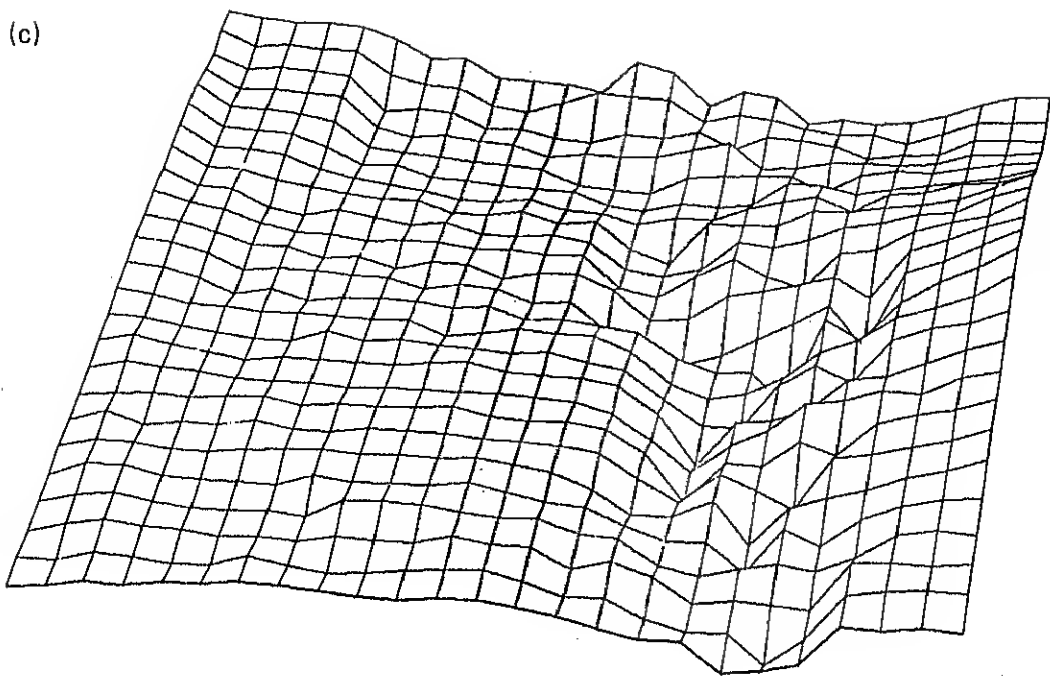
(d)
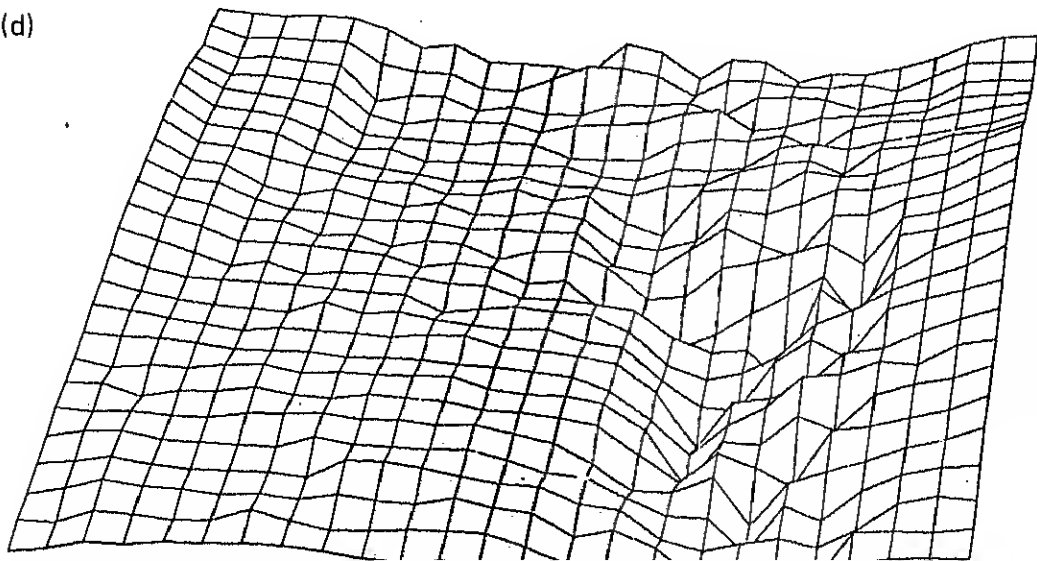
on the physics of turbulence than is the latter. Closure models are therefore more easily extended to the more complex meteorological situations in which formulation of a realistic eddy viscosity parameter becomes a near-impossible task. On the other hand, the disadvantage of a full-closure model is its relative complexity in comparison to those based on simple eddy viscosity parameterizations. To reduce this problem, efforts have been made to simplify the closure model (Mellor and Yamada, 1974).

Termed a "Level 2.5" model, this simplified closure scheme requires the prognostic solution of only a turbulence-energy equation and a "master length-scale" equation (Mellor and Yamada, 1977); the remaining second-moment equations are reduced to a set of algebraic relations in which tendency, advection, and diffusion terms are omitted. Although it is considerably simplified, the Level 2.5 model retains the essential features of the full-closure model. A one-dimensional version has been described and tested in a simulation of the Wangara boundary-layer data (Yamada, 1977); the results compare favorably with those obtained earlier by Yamada and Mellor (1975) with a higher level model. More recently, Miyakoda and Sirutis (1977) have included the Level 2.5 closure method in their atmospheric global circulation model which has made it possible to run the model successfully without the so-called dry convective adjustment, thus eliminating the spurious surface cooling previously caused by the convective adjustment.

The present version of the Level 2.5 model (Yamada, 1978a) incorporates recently proposed ensemble cloud cover statistics based on a Gaussian probability function (Sommeria and Deardorff, 1977; Mellor, 1977). More recently, the latest version of the model has been used to simulate the atmospheric boundary layer over the tropical ocean (Yamada and Mellor, 1979) and three-dimensional airflow over a large industrial cooling pond (Yamada, 1979a). It is a minor modification of this three-dimensional model that has been used here to study the effects of complex terrain on dynamics of airflow (Yamada, 1978b) and pollutant dispersion (Yamada, 1979c).

The governing equations are the (1) equation of motion for the horizontal wind components; (2) conservation equations for the liquid water potential temperature and total water, which are quasi-conservative quantities even when condensation occurs; (3) conservation equations for turbulence energy and a master length scale; and (4) the hydrostatic equation. These basic equations are transformed into a terrain-following coordinate system.

As a first step toward more realistic topography a Gaussian hill 500 m
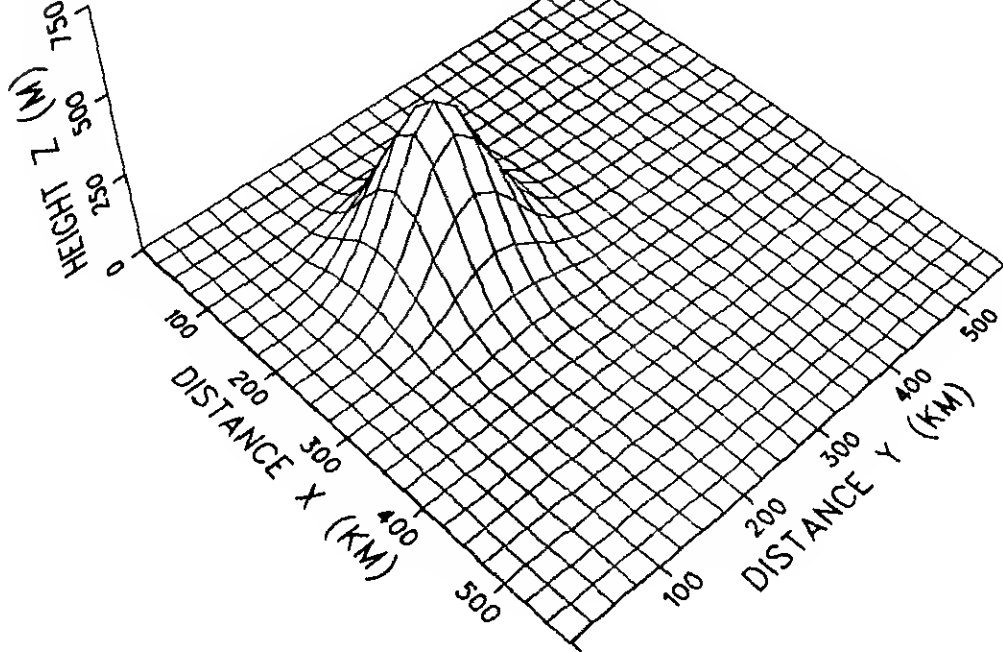
FIGURE 7.19 A Gaussian mountain used in early second-order closure modeling studies. The peak of the mountain is at z = 500 m.

dispersion over nonhomogeneous terrain. Preliminary analyses of the simulation for a stable atmosphere indicate complex effects on airflow; wind speeds are accelerated and decelerated due to the presence of the mountain (Figs. 7.20 and 7.21); maximum subsidence (2 m s^{-1}, not shown here) occurs approximately 3.5 km above the downward slope of the mountain, with much weaker maximum upward motion (0.2 m s^{-1}) over the surrounding area. Air directly over the mountain is also much warmer (by about 10°C, Fig. 7.22) and drier by about 2 g kg^{-1}.

Figure 7.23 shows simulated concentration profiles in a vertical plane through the diagonal A-B in Fig. 7.19. Contour values in Fig. 7.23 are normalized by the maximum value at the inflow lateral boundary. Concentration at the inflow boundary is nearly uniform below 1.5 km and decreases almost linearly with height above that level. Vertical gradients of concentration profiles in the surface layer are due to deposition at the surface. Deposition velocities were computed from the formula by Wesely and Hicks (1977) for sulfur dioxide and similar gases. Concentration decreases considerably on the lee side of the mountain.
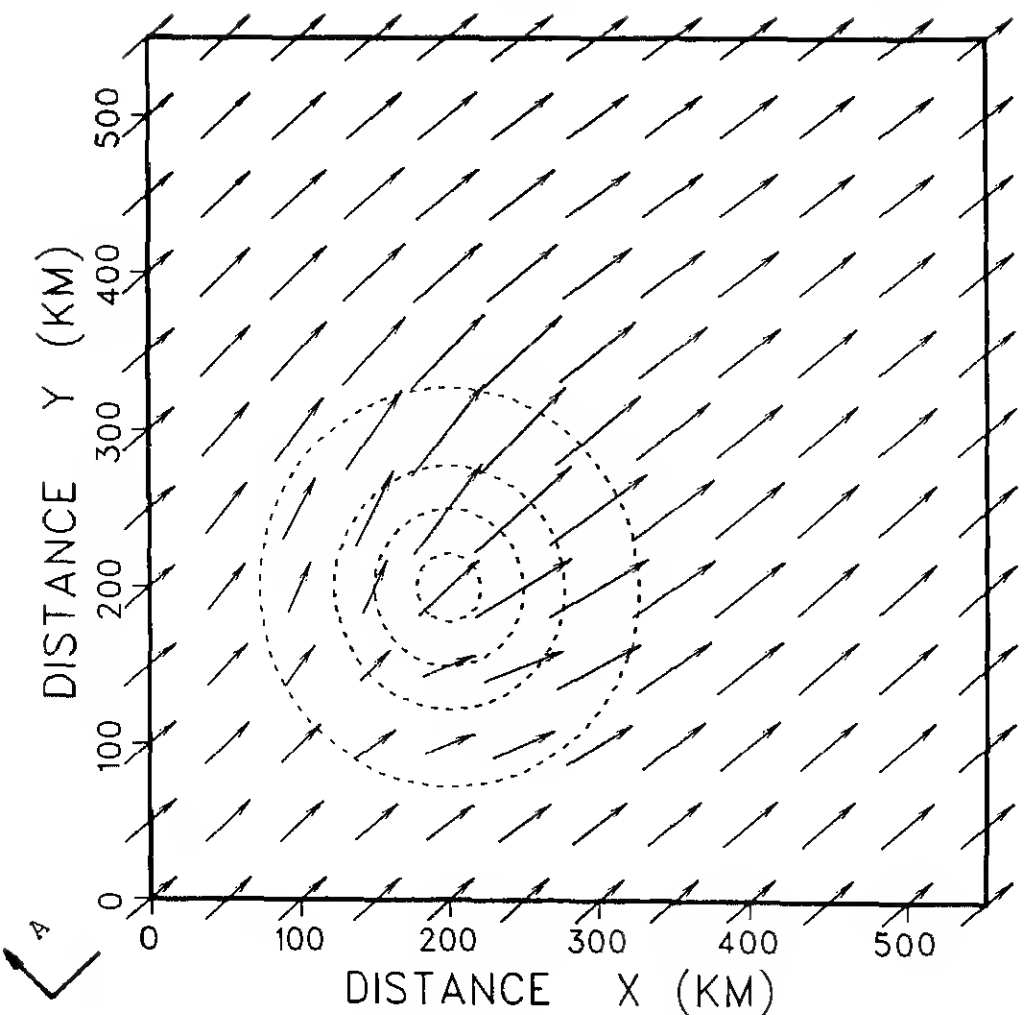
FIGURE 7.20   Horizontal wind vectors at 1000 m above sea level for a
single Gaussian mountain. Terrain is contoured by dashed
lines with an increment of 150 m. The lowest contour is
at z = 20 m.

higher levels by subsidence. Air in the layer below 2.5 km appears to be
cleaner than at the inflow boundary mainly due to subsidence and/or
deposition of the pollutant at the surface. On the other hand, air in the
layer above 2.5 km has a higher concentration than at the inflow
boundary, except in the regions directly over the crest. This is due to
the vertical transport of highly polluted air by the updraft. Upward
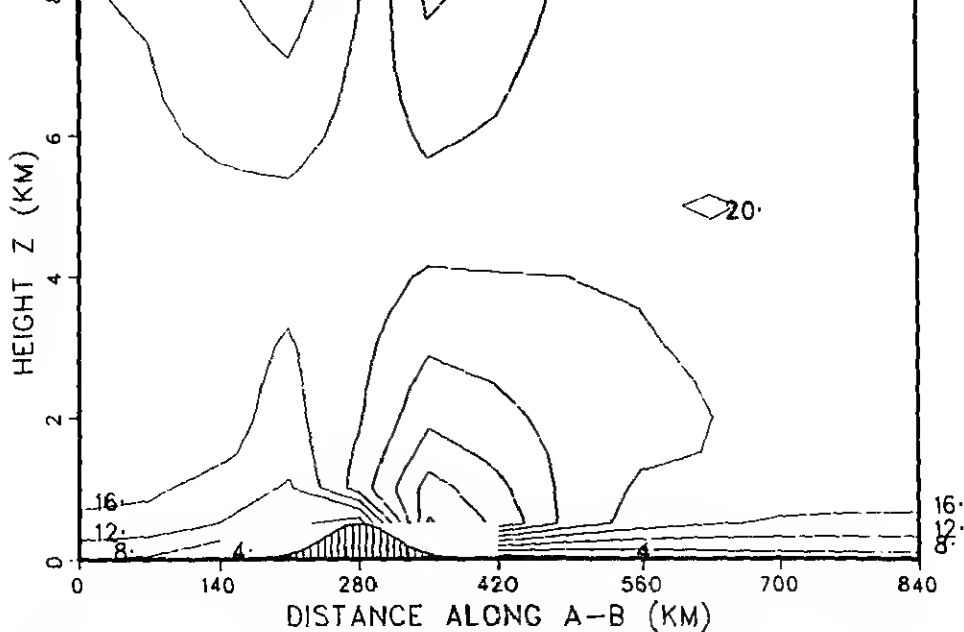
FIGURE 7.21 Distribution of horizontal wind speed (m s^{-1}) for the stable case in a vertical plane through the diagonal A-B in Fig. 7.20.

An additional simulation has been conducted under the same initial and boundary conditions but under unstable stratification. In this second case, surface temperature is increased to 20°C from 15°C used in the previous stable case (Case 1). Vertical profiles for the simulated mean variables for Case 2 are much more uniform than in Case 1 due to greater turbulent mixing: for example, a maximum wind simulated in the lee of the mountain for the unstable atmosphere has been reduced to 80% of the maximum simulated in Case 1. However, wind speed simulated in the surface layer for Case 2 has increased considerably compared with that in Case 1 due to greater momentum transport from upper layers.

The simulated concentration profiles for Case 2 are shown in Fig. 7.24. Major differences in the concentration for the unstable (Fig. 7.24) and stable (Fig. 7.23) conditions appear to occur in the surface layer downwind of the mountain. Concentration for the former is considerably larger than that for the latter mainly due to fumigation. Higher concentrations in the layer directly above have been transported downward by turbulent mixing.
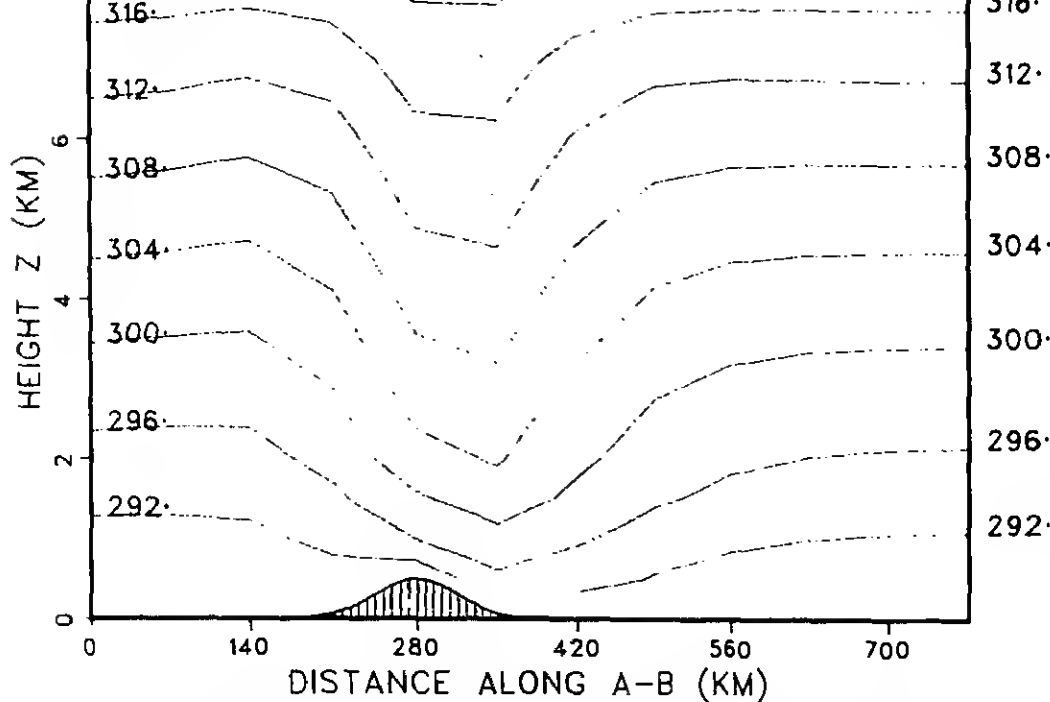
FIGURE 7.22 Distribution of the potential temperature (K) in a vertical plane through the diagonal A-B shown in Fig. 7.20.

surface (Fig. 7.26) are perturbed more strongly than those for a single mountain (Fig. 7.20), because more air is blocked by the mountains.

The model is currently being modified to include solar radiation in order to produce diurnal variations for the airflow. It is intended to test the simulation against observations in the near future.

7.4.2 The BNL-Kreitzberg Mesoscale Model[*]

A three-dimensional primitive equation model with a one dimensional sequential plume cumulus model for convective parameterization has been implemented in a preliminary form at BNL. The model is hydrostatic with fully moist physics, including maintenance of rain water, cloud water and water vapor at all levels. Liquid water can be present in either the liquid or ice stages following the parameterization developed by Kessler (1969). The vertical coordinate is an expanding
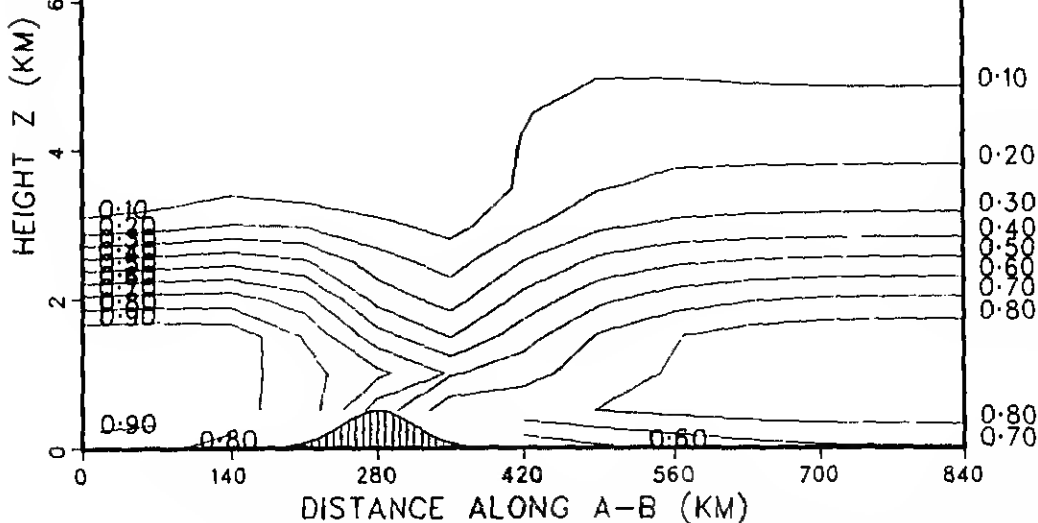
FIGURE 7.23 Distribution of normalized concentration for the stable case in a vertical plane through the diagonal A-B in Fig. 7.20.
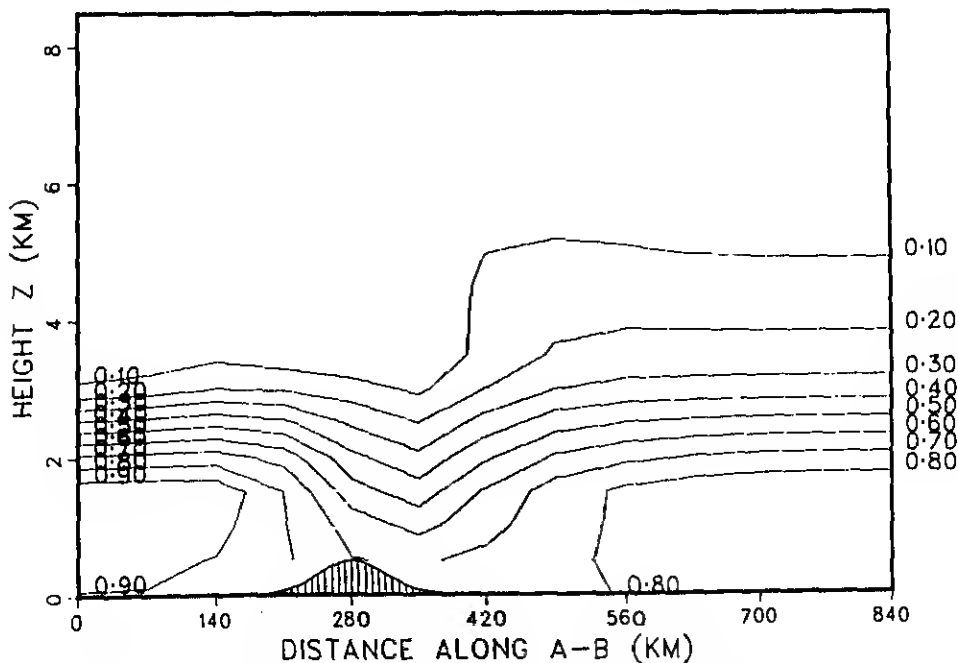
FIGURE 7.24 Same as Fig. 7.23 but for the unstable case.
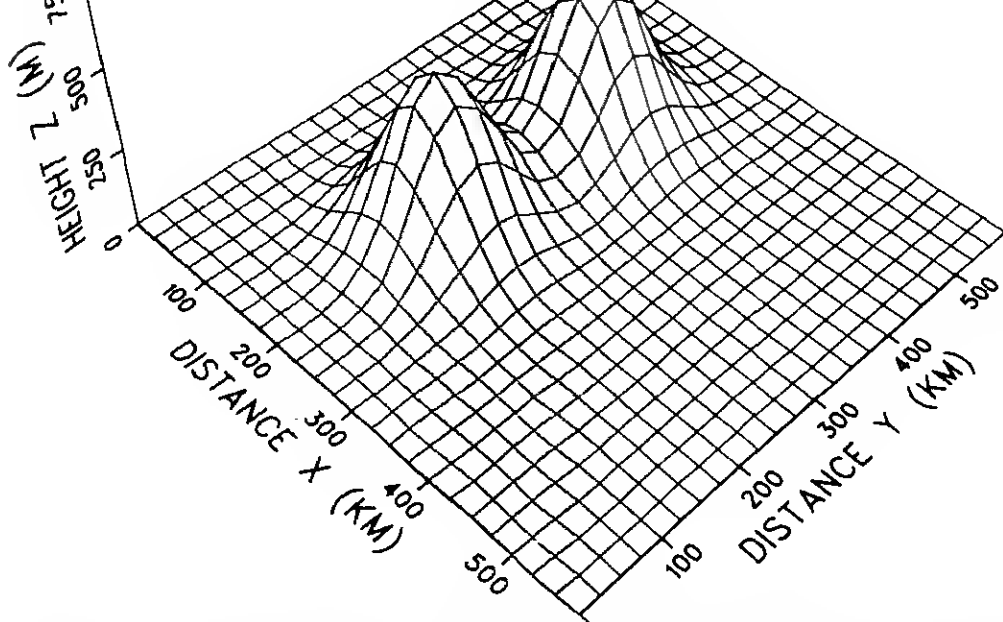
FIGURE 7.25 Two Gaussian mountains that are constructed by adding
another mountain to the one in Fig. 7.19. The distance
between the peaks is 400 km.

sigma-z system. This permits better resolution in the boundary layer and
is terrain following. The numerical technique is fourth order centered
finite difference in the horizontal, second order centered finite
difference in the vertical, and leap frog in time with smoothing to
prevent splitting of the solution. A more complete documentation of the
model characteristics can be found in Kreitzberg and Perkey (1977),
Kreitzberg et al. (1974), or Perkey (1976).

In an effort to aid implementation of the model at sites other than
where it was developed (NCAR), a programming philosophy known as the
Limited Area Mesoscale Prediction System (LAMPS) has been adopted.
There are three main levels of programs in this LAMPS system: analysis
codes, the prognostic model, and post processors. The analysis codes are
used to get raw data from observations and larger models into suitable
form for use in the prognostic model. The post processors are the codes
that examine the results of the model run or use the results in further
computations.

As implemented at BNL, the three-dimensional model has been run in
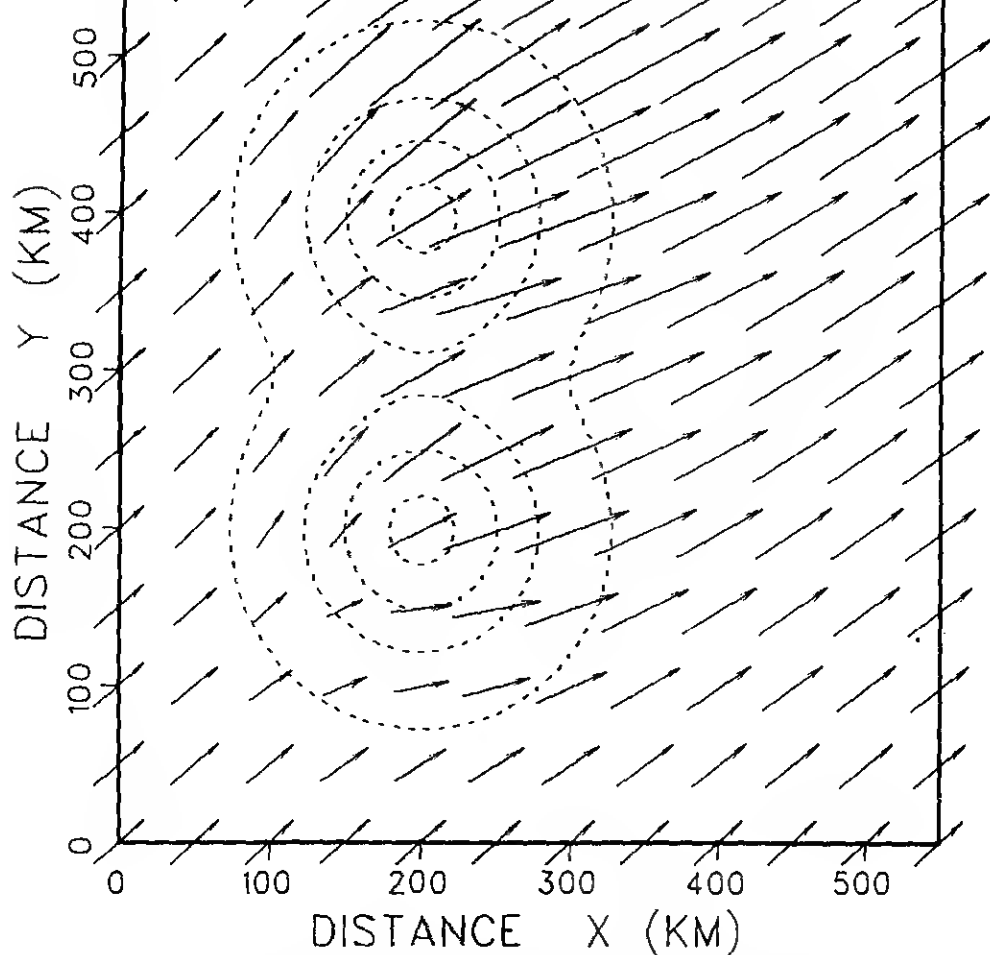
FIGURE 7.26 Horizontal wind vectors at 1000 m above sea level for twin mountains. Terrain is contoured by dashed lines with an increment of 150 m. The lowest contour is at z = 20 m.

using data from the NASA-sponsored AVE II experiment of May 11 and 12, 1974.

A model to analyze the three-dimensional trajectories and cleansing rates from the primitive equation (PE) model has also been run at BNL. Because the three-dimensional PE model includes the fully moist physics and detailed vertical velocity fields, the trajectories are more detailed than those obtained from conventional data. The cleansing is defined as the amount of precipitation (mm) falling through the air parcel as it

vertical velocities in calculating trajectories. Trajectories from the model output with greater horizontal resolution traverse smaller horizontal distances because of greater vertical displacement. Air parcels often start from lower heights where the winds are weaker. This also tends to keep the parcel in the rain zone for a longer period of time and therefore generally results in more cleansing. Further details of this trajectory experiment can be found in Kreitzberg and Leach (1978).

A modification to this trajectory code has also been made. It is now capable of doing jet streak analysis, i.e., parcels passing through a particular point can be followed as a function of time. This type of analysis could be particularly valuable for air pollution studies, especially for continuous sources that can be looked at in a "snapshot" sense. Work is continuing to include the diffusion of atmospheric contaminants within the trajectory-streak line model. Future research could involve calculating the scavenging of the pollutants by the rain, especially since the details of the moisture profiles exist in the PE model output. The complex problem of formulating a precipitation scavenging mechanism for aerosols will have to be addressed, but as a first pass a simple parameterization scheme, based on the cleansing as defined before, and the pollutant concentration could be utilized.

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It is no longer sufficient to know only the details of the emissions and transport of pollutants. Understanding the nature and extent of the transformation of the pollutants from one chemical form to another has become exceedingly important, especially in the case of sulfur where the aerosol sulfate transformation product has been identified as a more serious health hazard than the originally emitted gaseous sulfur dioxide (Amdur et al., 1972). Consequently, in recent years much attention has been devoted to understanding the transformation of sulfur pollutants.

Laboratory studies have been directed to the study of homogeneous gas phase reactions. The hydroxyl free radical has been identified as especially important and the rate constant with sulfur dioxide has been measured (Castleman et al., 1975). The laboratory studies have also demonstrated the importance of heterogeneous reactions between sulfur dioxide and particulate matter to form sulfate (Judeikis et al., 1977).

Much attention has been directed to studying the transformation of sulfur dioxide in power plant plumes. Transformation studies in power plant plumes are looked upon as important in their own right and also as a model for what happens in the atmosphere as a whole (Newman, 1977). Earlier studies indicated oxidation rates in excess of 10% per hour, but it is now considered that in general the high oxidation rates presented were an artifact of poor measurement capabilities. More recently it has been observed that the extent of oxidation in power plant plumes seldom exceeds 5% even when plumes are followed for 200 minutes (Forrest and Newman, 1977a). Most of the studies were performed during the atmospherically stable condition of early morning or evening hours. Higher oxidation, with rates of 3 to 4% per hour, have been found during midday measurements (Husar et al., 1978)

Oxidation rates in urban plumes have been found to be higher than those observed in power plant plumes (Alkezweeny and Powell, 1978; Husar et al., 1978) with rates as high as 10% per hour especially during full daylight conditions. A strong case can now be made for the importance of homogeneous photochemical oxidation of sulfur oxide, however heterogeneous reactions involving particles also appear important. Understanding and inclusion of both mechanisms is important in elucidating the role of the transformation of sulfur pollutants in the MAP3S program.

8.1 MECHANISTIC STUDIES OF POLLUTANT TRANSFORMATION

of course, be interested in the results of these efforts while at the same time sponsoring highly focused activities for which DOE funded groups have specialized capabilities.

8.1.1 Isotopic Ratio Measurements

One particular area where we believe MAP3S could make an important contribution involves investigating the potential for determining the origin of atmospheric sulfate by study of the isotopic composition of the sulfate in particulate material and precipitation and that of its presumed percursors (H_2O, SO_2) in the atmosphere. During the last three years this capability has been demonstrated in laboratory investigations. As a part of the MAP3S program, appropriate samples have been collected on a regular basis over a two-year period (1975 and 1976) at ANL and subsequently analyzed. The data obtained are summarized in Figs. 8.1 and 8.2 where the ^{18}O content (expressed in del units which are the deviation in parts per thousand of the $^{18}O/^{16}O$ ratio of the sample from that of standard mean ocean water) of the various species is plotted against time.

The ^{18}O content in precipitation sulfate was found to vary seasonally and in phase with the corresponding ^{18}O content in precipitation water (Fig. 8.1). The ratio of the amplitudes of the ^{18}O-vs.-time curves indicated isotopic equilibration between aqueous SO_2 before oxidation. In contrast, the ^{18}O content of particulate sulfate (Fig. 8.2) appeared to vary randomly with season, although its yearly average approximately equaled that of sulfate in precipitation. If particulate sulfate and precipitation sulfate were formed by the same heterogeneous mechanism in clouds, one would expect that their isotopic composition and ^{18}O seasonal variations would be the same. These observations indicate that their isotopy is different. This can be explained either as a result of a new mixture of water vapor and particulate sulfate being established over long residence times and transport distances (thereby separating the sulfate from the water vapor environment in which it was formed) or as evidence that the origins of particulate sulfate and precipitation sulfate are different. This latter explanation, while possible, seems somewhat unlikely since the long term average ^{18}O content of particulate and precipitation sulfate are very nearly the same. Further work is needed to sort out these possibilities.

In a related MAP3S experiment, oxygen-18 analyses were made on samples of water vapor collected at ground level and at cloud-base and above-cloud-base levels (using PNL aircraft). There is some indication that the ^{18}O content of water vapor decreased with increasing altitude (Fig. 8.3). Since the isotopic character of atmospheric water contributes heavily to that of sulfate formed by the mechanism of aqueous oxidation
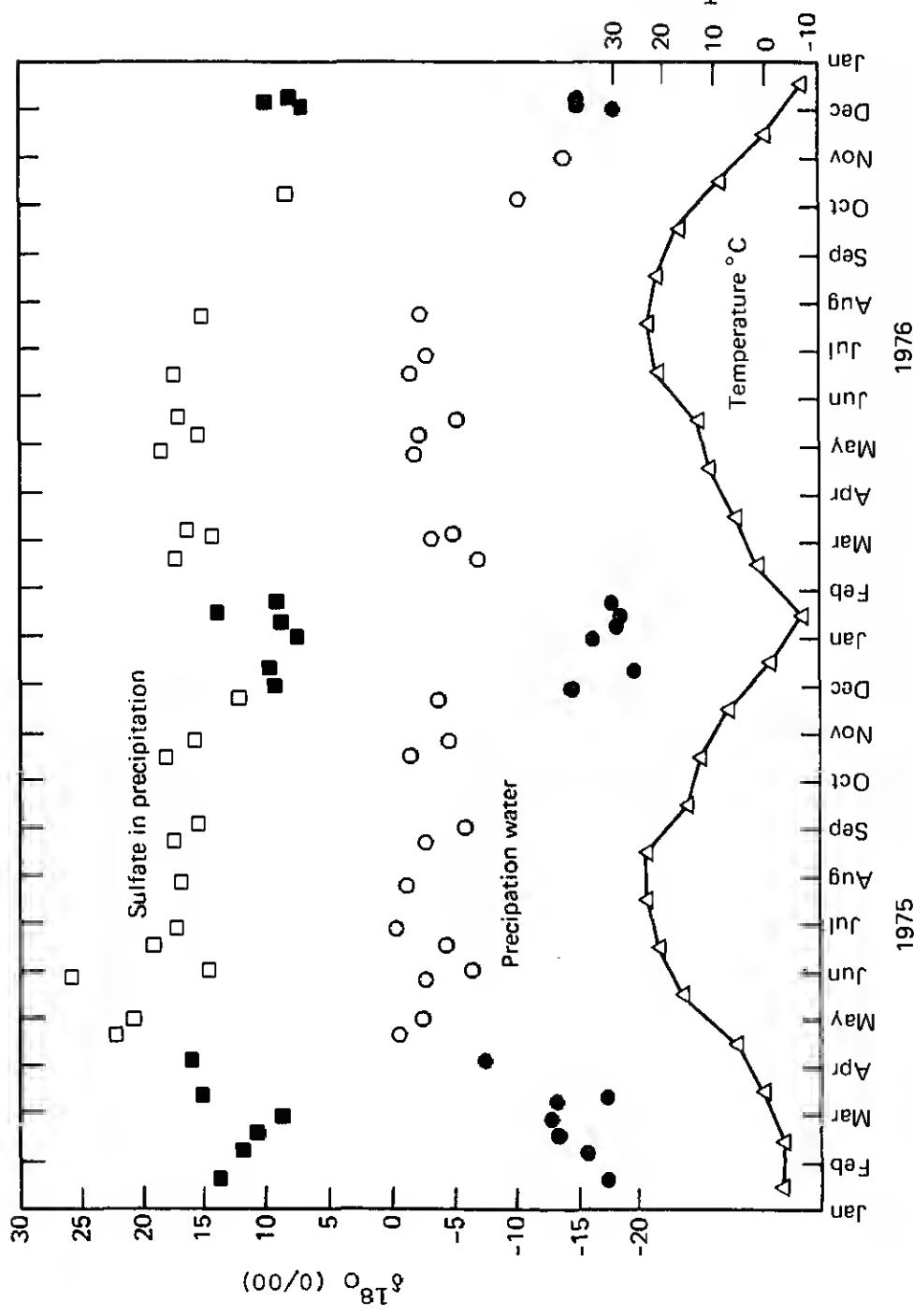
FIGURE 8.1 Isotopic results for dissolved sulfates and water in precipitation, and average monthly temperatures at Argonne, IL, 1975 and 1976. Solid data points denote snow samples.
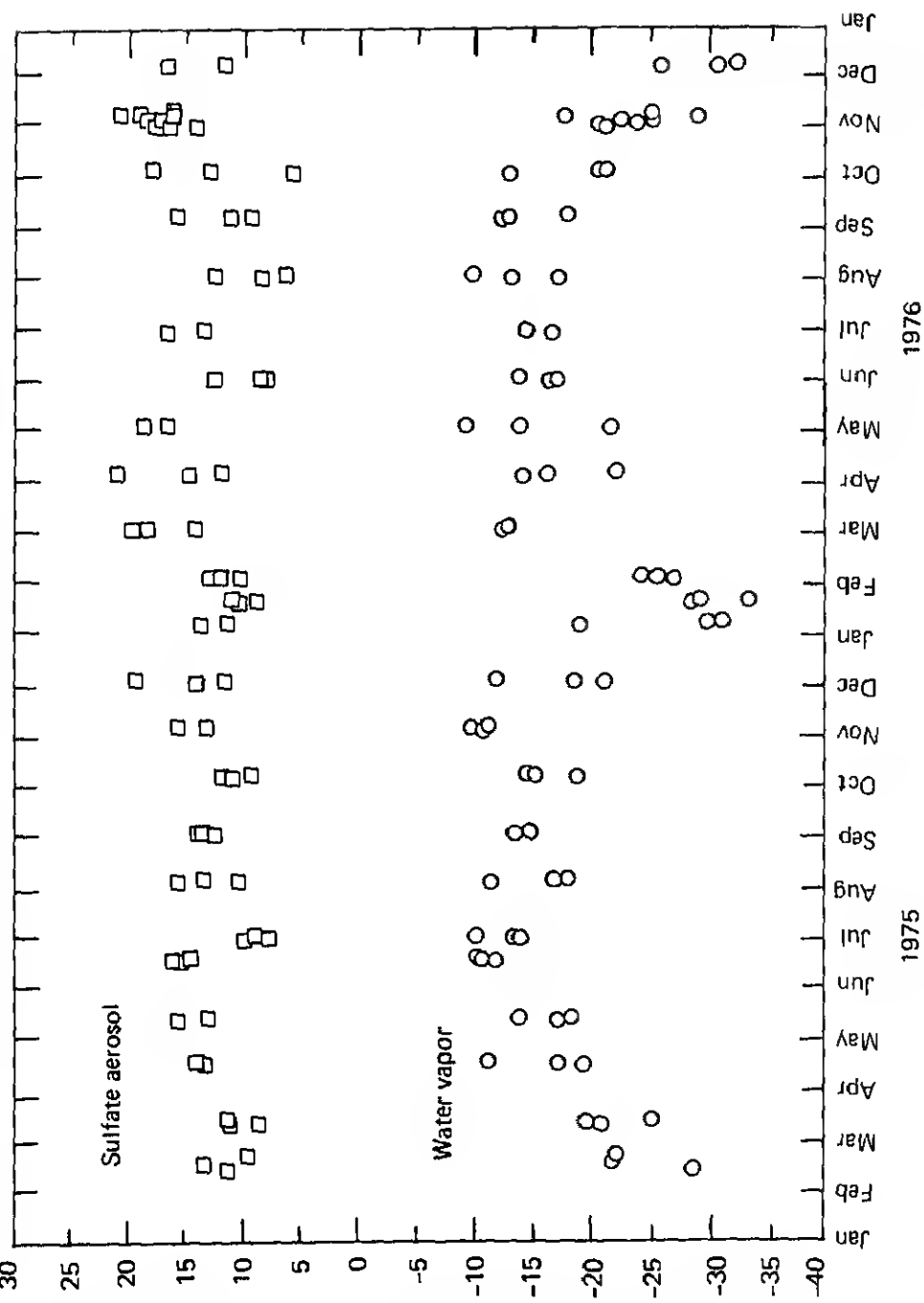
FIGURE 8.2 Isotopic results for particulate sulfates and water vapor at Argonne, IL, 1975 and 1976.
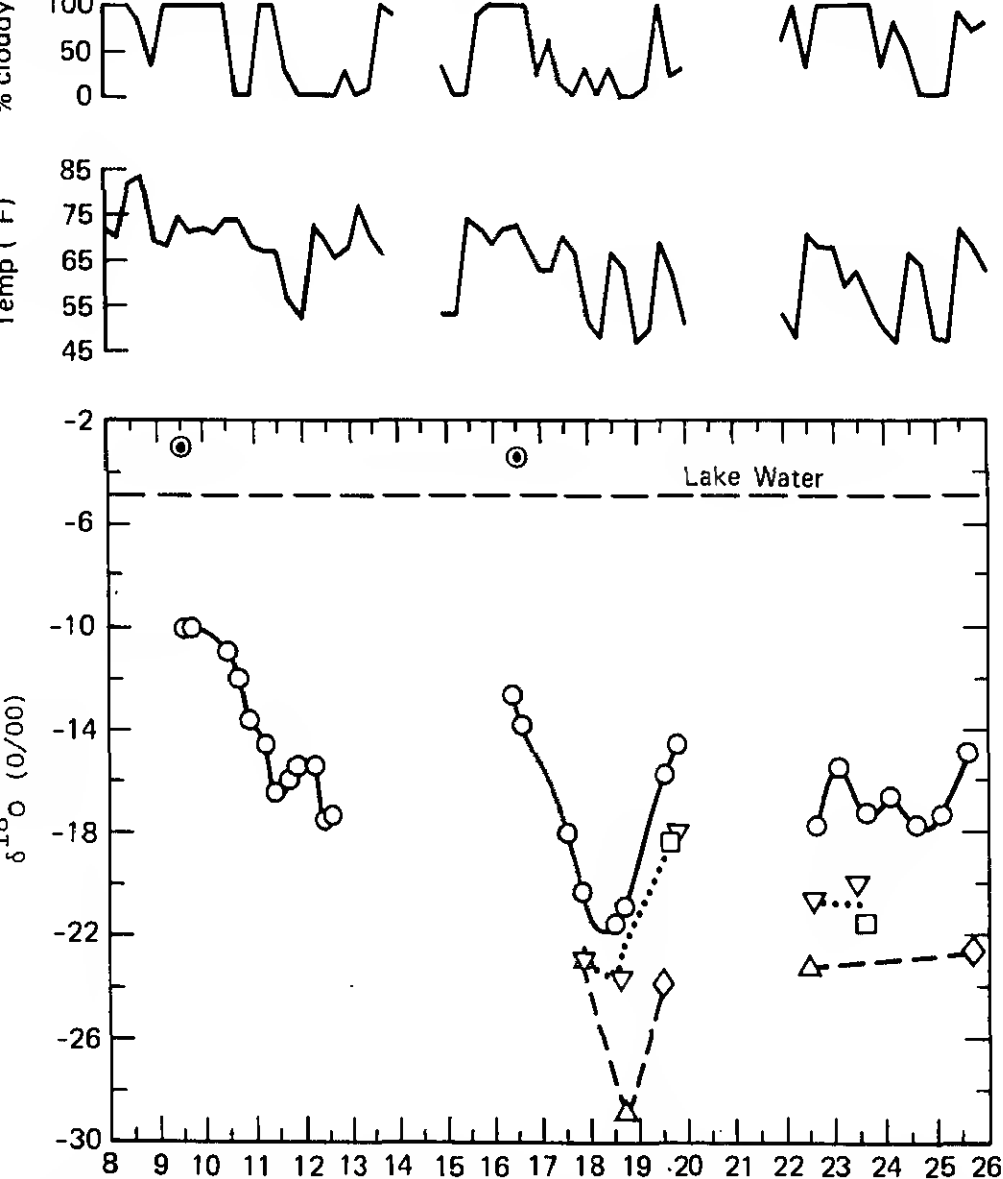
FIGURE 8.3 Isotopic results for water vapor (at ground level and higher elevations), and lake water at Muskegon, MI, August, 1977. Legend: ⊙, rain; ○, water vapor (wv) at ground level; ∇, wv in mixing layer over land; △, wv above mixing layer over land; □, wv in mixing layer over lake; ◇, wv above mixing layer over lake.

atmospheric samples of particulate sulfate and water vapor that were collected simultaneously during a 6-day period at three sites (St. Louis, MO; Auburn and Glasgow, IL) spaced 100 km apart in July, 1975. Consistent concerted variations in isotopic and concentration (collection rate) results (Figs. 8.4 and 8.5) were observed for the three sites near St. Louis, demonstrating an apparent regional impact on the quality and quantity of particulate sulfates in the atmosphere. The regional effect was confirmed by calculated back trajectories of the air masses reaching the sampling points (Figs. 8.6 and 8.7). In this experiment, the ^{18}O content of particulate sulfate varied inversely with concentration, indicating that sulfates of heavy loadings differed in origin, and probably in mechanism of formation, from those of light loadings.

Although the hydrolysis-oxidation mechanism apparently dominates in the transformation of SO_2 to the sulfates that are found in precipitation, more than one mechanism may be prominently involved in the formation of particulate sulfates. The relative importance of such mechanisms therefore needs to be differentiated and defined with respect to season and location.

Oxygen-18 analyses are being made of continuous week-long samples of particulate sulfate, sulfur dioxide, water vapor and dustfall for an entire year. Continuous sampling may afford better resolution of the presence of more than one mechanism of transformation than did the three samples per month collection system used in the previous two-year experiment. Laboratory experiments are being continued in the ^{18}O study of SO_2 transformation by mechanisms of hydrolysis-oxidation and oxidation-hydrolysis under various experimental conditions.

8.1.2 Laboratory Studies

Laboratory evaluations of some other important transformation mechanisms have also been conducted. Hitchcock (1976) has suggested that atmospheric oxidation of hydrogen sulfide of biogenic origin may be a significant source of atmospheric aerosol sulfate. The contribution of this process to the atmospheric sulfate burden would be substantially greater if H_2S were oxidized directly to sulfate than if SO_2 were an intermediate product because of competitive paths for the removal of the SO_2. The principal atmospheric reaction of H_2S is with hydroxyl radical OH to form the HS radical (Sprung, 1977). Work at Brookhaven (Thiemens and Schwartz, 1978) has established that the fate of HS radical under atmospheric conditions is to form SO_2 with essentially unity yield. This work strongly diminishes the potential contribution of H_2S to ambient sulfate concentrations, and additionally rules out the possibility of elevated local concentrations of such biogenic sulfate in view of the relatively long residence times of both H_2S and SO_2.

$\delta^{18}O$ (0/00) along the vertical axis, July 1975 along the horizontal axis, with labels "Low pressure", "Frontal system", "Glasgow", "Auburn,", and "St. Louis".
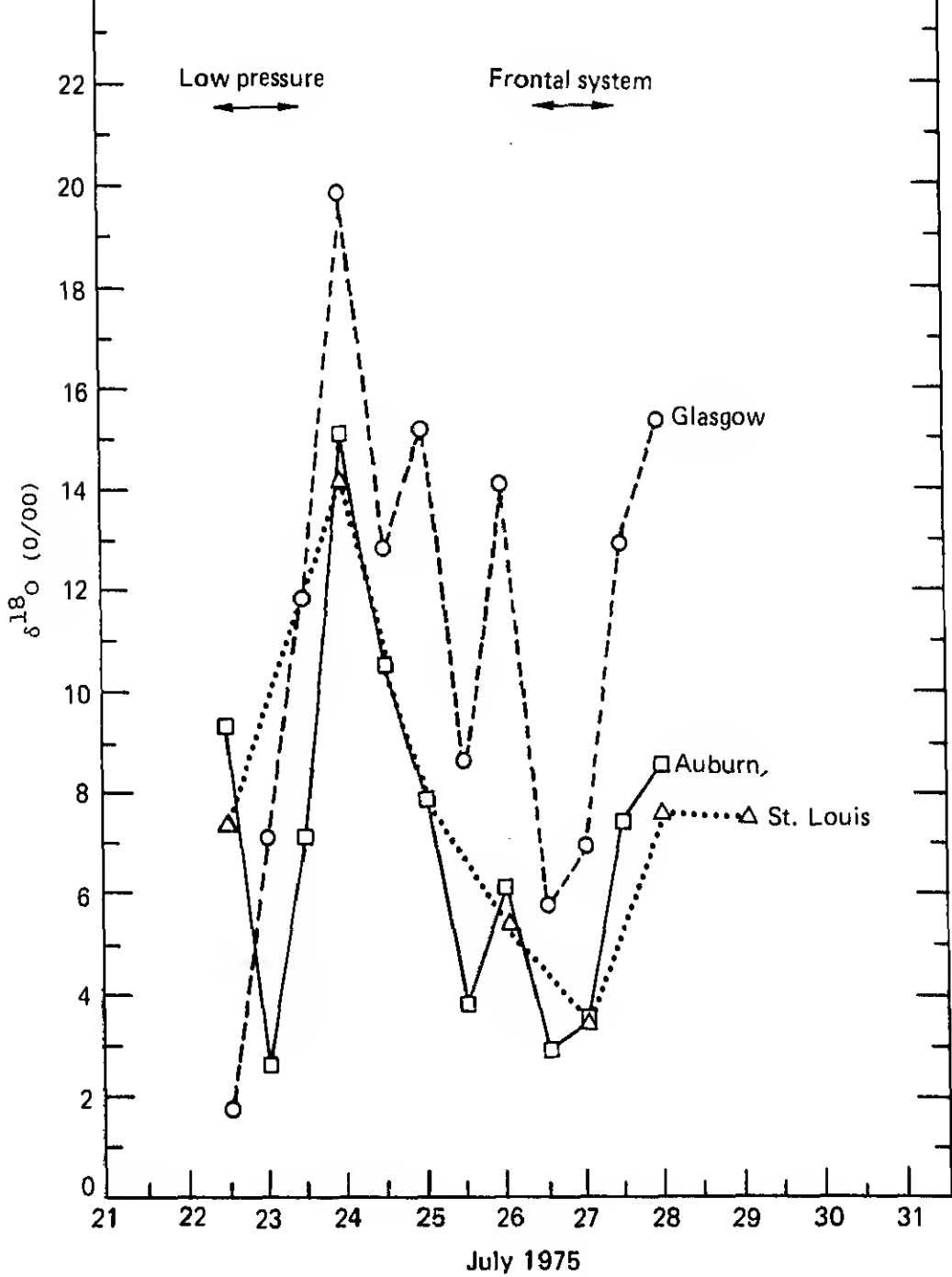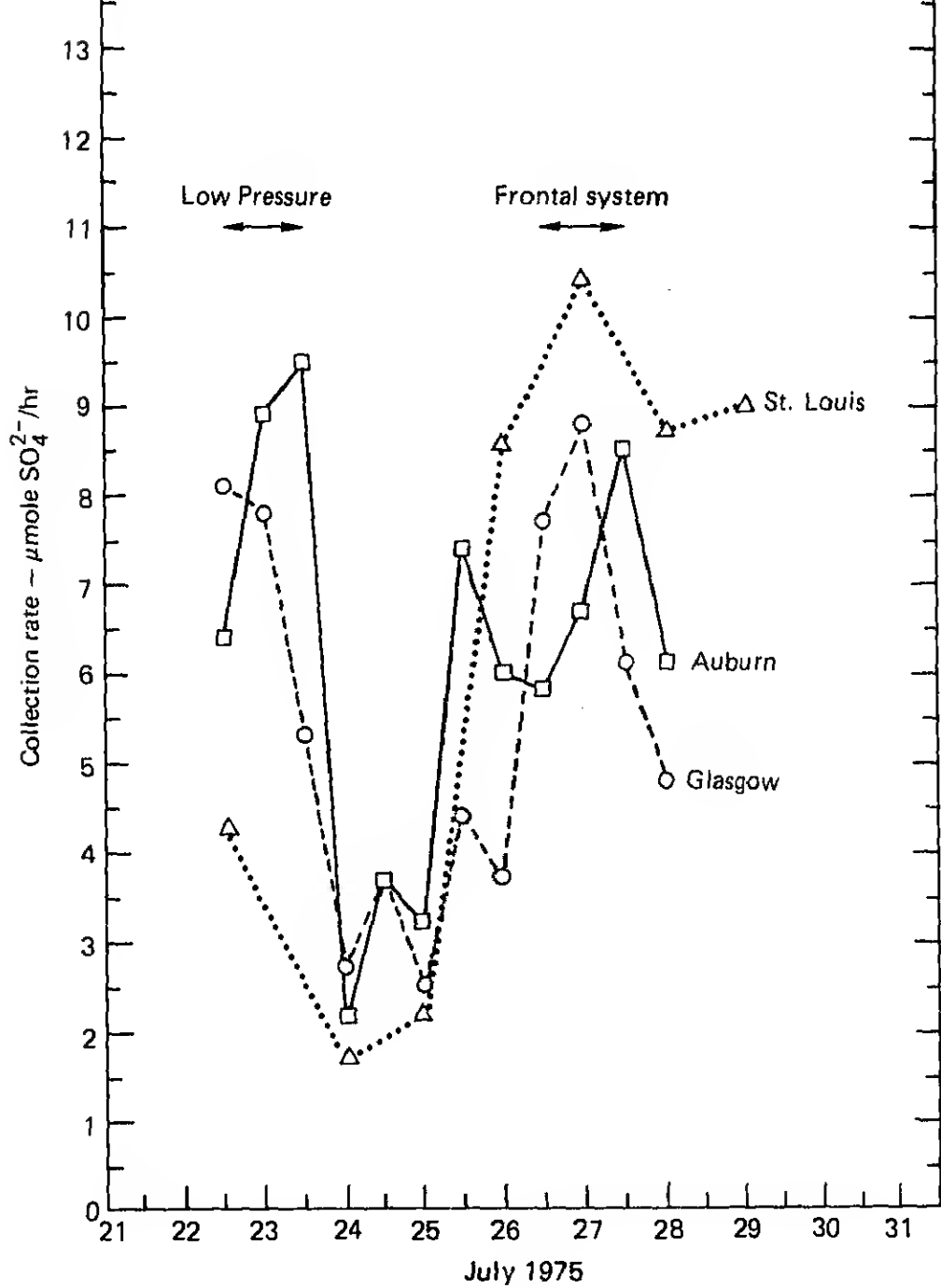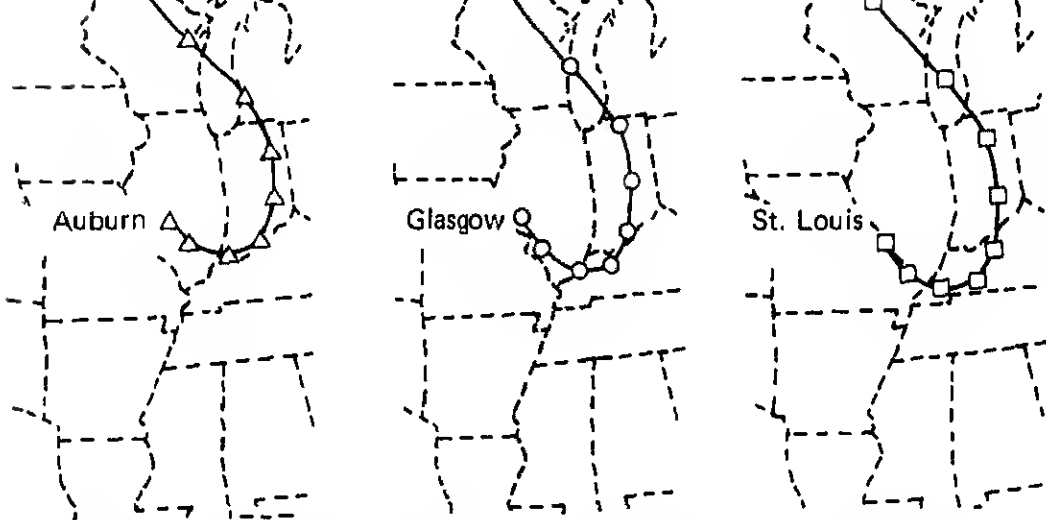
FIGURE 8.6 Back trajectories (6-hour intervals) from midnight, July 23-24, 1975.
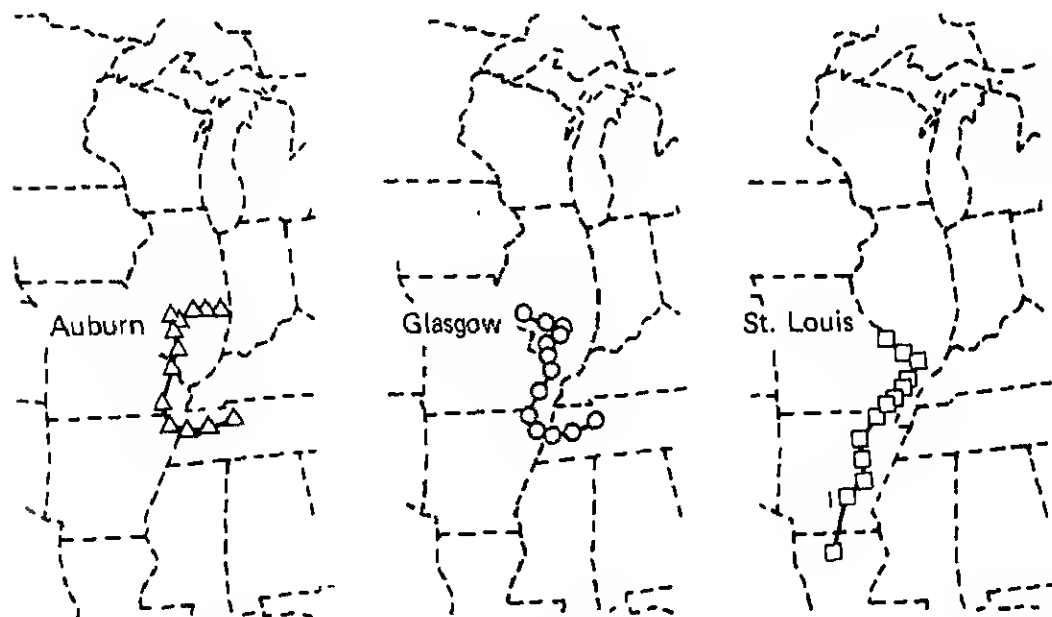
FIGURE 8.7 Back trajectories (6-hour intervals) from noon, July 26, 1975.

or mixed forms. Such inorganic salt aerosols exhibit the properties of deliquescence upon exposure to moisture. The phase transformation from a solid particle to a saline droplet usually occurs suddenly when the relative humidity in the atmosphere reaches a value specific to the chemical composition of the aerosol particle. Research at BNL (Tang, 1976) has shown that the growth of a mixed-salt aerosol by water vapor condensation may go through several stages of multi-phase equilibria before its complete dissolution to form a homogeneous solution droplet. The growth characteristics and associated thermodynamic properties of the mixed chlorides, sulfates, and nitrate aerosols have been measured, and the results compare well with theoretical predictions.

8.2 TRANSFORMATION IN POWER PLANT PLUMES

Because other sources of support have been available to both BNL and PNL the MAP3S effort in power plant plume studies has been limited largely to analysis and interpretation of results. The following two sub-sections describe the status of research by each of the two groups involved.

8.2.1 Plume Studies Performed by BNL

EPRI, LILCO and ESEERCo supported BNL to conduct a comprehensive study of the plume from an oil-fired power station. This program involved approximately 50 aircraft missions and at least 15 stack sampling experiments (see also Sec. 3.1). An experimental design has been developed that is gathering data to test the prevailing plume chemistry models. With about 75% of the experimental program complete the data indicate that 50% or more of the sulfate measured in plumes is primary sulfate emitted from the plant. Sulfur dioxide to sulfate conversion rates in plumes appear to be no greater than 1%/hr under most conditions; however, higher rates have been observed on a few occasions. Experimental measurements of strong acid in plume aerosol suggest that a principal component of plume sulfate may be sulfuric acid. Attempted correlations of plume conversion rates with meteorological conditions indicate some correlation between sulfate formation and solar radiation.

The BNL aircraft was also involved in the Tennessee Plume Study of the EPA STATE Program. The Cumberland coal-fired power plant plume was the subject of an extensive series of plume measurements. Initial results indicate conversion rates similar to the results cited above; however, strong acid content appears to be markedly lower in the Cumberland plume. Although meteorological conditions were far from

A series of experiments were performed (Forrest et al., 1979) during August 1976 and February 1977 at the oil-fired Anclote power plant of the Florida Power Corp., Tarpon Springs, Florida, which operated without any particulate controls and presumably with high particulate emissions (subsequently found to be relatively low). The purposes of the mission were to evaluate the significance of the heterogeneous catalysis mechanism, to gain further insight into the relationship between plume sulfate formation and plant operating parameters (e.g., excess oxygen) and meteorological conditions upon oxidation rates. In addition, studies were made of particulate ammonium and nitrate formation in the plume and sulfate drop-out beneath the plume. Concurrent with BNL's plume measurements in February, personnel from EPA's Stationary Source Emissions Research Branch analyzed flue gas as part of their stationary source measurements program.

Plume samples at varying downwind locations were obtained by means of a high-volume filter pack assembly consisting of a quartz pre-filter to collect particulate matter and K_2CO_3-impregnated cellulose filters to absorb SO_2. Particulate samples were processed for sulfate, titratable strong acid, ammonium and nitrate; cellulose filters were analyzed for SO_2; sulfur isotope ratio ($^{34}S/^{32}S$) analyses were performed on some of the SO_2 samples. Background samples were taken and results subtracted from plume concentrations.

Plume sulfate dropout was evaluated in four tests wherein samples were taken within and directly beneath the plume at fixed locations. Adverse weather conditions caused cancellation of two runs. However, in the other two runs, particulate sulfate concentrations beneath the plume exceeded background sulfate by factors of two to three, providing positive evidence for dropout.

Operational oxygen levels during fuel combustion were varied over a five-day period in the February experiments. Flue gas sulfuric acid measurements by EPA showed a direct relationship with excess furnace oxygen. Plume sulfuric acid concentrations (expressed as ratios to total plume sulfur) as indicated by particulate strong acid measurements revealed a similar dependency upon oxygen levels. Total particulate sulfate in both flue gas (EPA) and plumes (BNL) also varied directly with excess oxygen.

Reaction of NH_3 with SO_2 and/or H_2SO_4 as the plume progressed downwind was examined by analysis of aerosol NH_4^+ from quartz filters and expressed as NH_4^+/total S ratios. An overall positive slope of this ratio with distance was discerned. Some runs showed a sharply delineated trend with definitive increments as the plume aged, whereas

quantities of nitrate, outside of two locations, pointed toward virtually no change from initial nitrate concentrations as expressed by NO_3^-/total S ratios. Conceivably some gaseous nitrate, HNO_3, may have formed, but this product was not detectable by our filter pack.

Conversion of SO_2 to sulfate as indicated by SO_4^-/total S ratio was generally within the 1-3% range with but two runs reaching levels > 3% (Fig. 8.8). The "pooled" average curve hovered around the 1.5-2% level, with virtually no change occurring from initial formation of sulfate with increasing distance or time of 50 km and 100 min respectively.

$^{34}S/^{32}S$ ratios (del values) were measured for samples with sufficient mass, and remained fairly constant for each run, substantially within the analytical precision of the procedure. Absence of change in the SO_2 del values indicated little if any oxidation between the first sampling
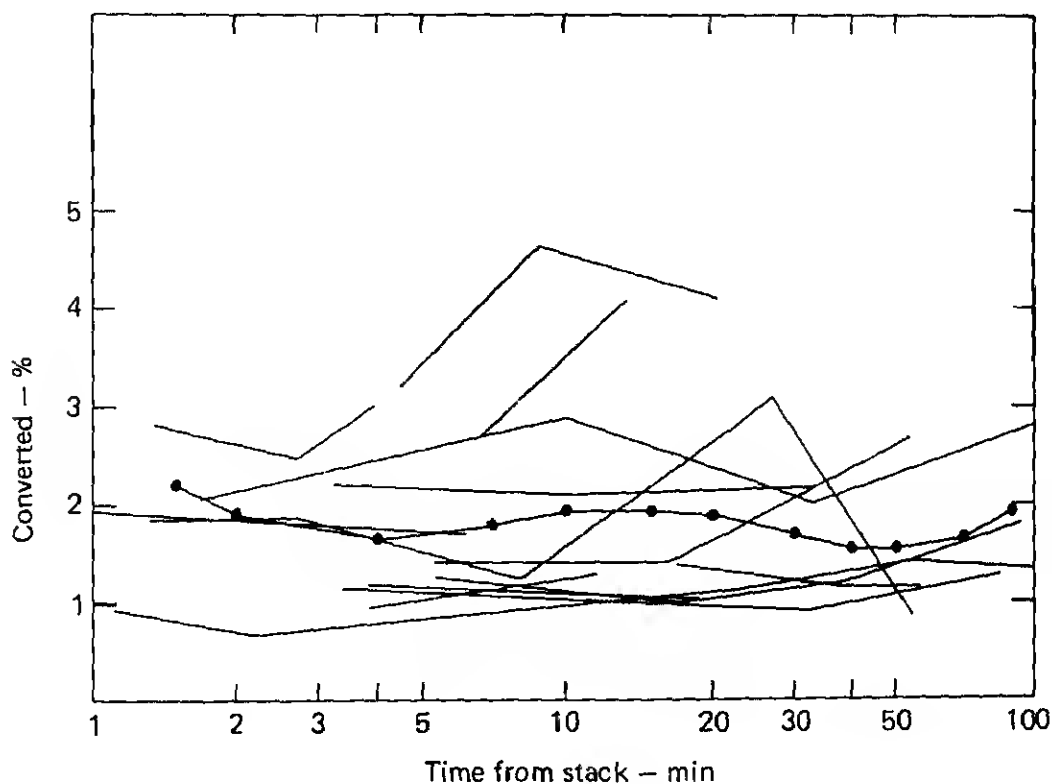
into discrete categories and the average % conversion for each group plotted against time from emission. Slopes were generally zero, indicating virtually no additional oxidation of SO_2, within our time frame, as a function of any of the above parameters.

The average SO_2 oxidation rates for all runs during August and February were 3.0% and 1.5%, respectively. Although average temperature, relative humidity and water vapor partial pressures were much higher for the August series, the influence of these meteorological parameters upon the observed difference was probably minimal. A more likely explanation is that the contribution of the fuel oil vanadium to the formation of primary sulfate during the combustion process was greater during August than during February.

8.2.2 Plume Studies Performed by PNL

Primary research emphasis in the PNL studies was placed upon transformations of sulfur and nitrogen oxides, with the principal objective of generating parameterized transformation relationships suitable for input to models currently being developed for the EPRI Sulfate Regional Experiment (Easter et al., 1979).

Extensive field measurements were performed in late spring and late fall of 1977 at two coal-fired and one oil-fired power plants; the Breed plant in Indiana, the Cobb plant in Michigan, and the Andrus plant in Mississippi. Plume measurements were obtained using the PNL instrumented DC-3 aircraft. Measurements included gas concentrations (SO_2, NO_x, O_3, NH_3, HNO_3, hydrocarbons), particulate composition ($SO_4^{=}$, NO_3^{-}, NH_4^{+}), and physical aerosol parameters. Source emission measurements were also performed. SF_6 tracer was also released into the plumes to allow better tracking. The resulting data, which include 140 hours of aircraft measurements, have been organized into a data base at EPRI.

Conversion and loss rates of SO_2 and NO_x were estimated using a variety of ratio techniques, and the results were analyzed using reactive plume models of varying complexity. A parameter-search technique was developed to utilize a reactive plume model to establish candidate conversion expressions for SO_2 transformations.

SO_2 was generally found to oxidize in power plant plumes at rates ranging from 0-3%/hr, depending upon insolation, plume dispersion, and ambient hydrocarbon concentration, as well as a variety of possible

significant than heterogeneous paths under the conditions observed. Nitrogen oxide data suffer from lower measurement sensitivity, but preliminary indications are that nitrate and nitric acid production proceeds quite slowly in plumes, although substantial total NO_x losses were sometimes observed. Although definite trends are apparent in the data, substantial additional analysis is required before their full benefit can be realized in the form of parameterized rate expressions.

In addition to these EPRI flights, DOE/MAP3S flights investigating urban plumes over Lake Michigan provided the opportunity for observation of distinct, imbedded power-plant plumes originating from individual power stations. One particular study is of particular interest in this regard. This is the observation of obvious ozone "bulges" in aged plumes as shown in Fig. 8.9.

Chemical reaction schemes applied in analysis of these results suggest that the observed phenomena are in reasonable conformance with theory (Miller et al., 1978). This is important to the development of a general sulfate-production model, owing to the mutual importance of several of these reactions to the generation of both sulfate and ozone.

8.2.3 Coal Fired Power Plants: Arid Conditions

In February 1977, in cooperation with the research group of Dr. Clyde Hill, University of Utah, the BYU group collected total aerosol samples by aircraft in the plume of a coal fired station in New Mexico that burns low sulfur western coal. The only S(IV) species seen in this source were apparently sluff-off products from the wet scrubber that presumably existed as $CaSO_3$ species. These labile sulfite complexes were detected in the stack but not in the plume samples. Unfortunately the amount of material available for analysis was insufficient to reliably define the plume S(IV) chemistry. Thus, no data are yet available on the transformation of more stable sulfite species that we have shown to exist in the plume of two other coal-fired stations studied (Eatough et al., 1978).

During the winter of 1977 and 1978 samples were collected from a coal fired power plant in Utah. Both organic and inorganic S(IV) species (10-50% of observed total particulate sulfur) were routinely seen on particles emitted from this plant. During August 1978, BYU personnel collected samples at three different distances from a coal fired power plant in Pennsylvania. S(IV) species were also routinely seen in similar amounts in these samples. Data analysis for samples collected at this site are not yet complete so conclusions on transformation chemistry cannot yet be drawn.
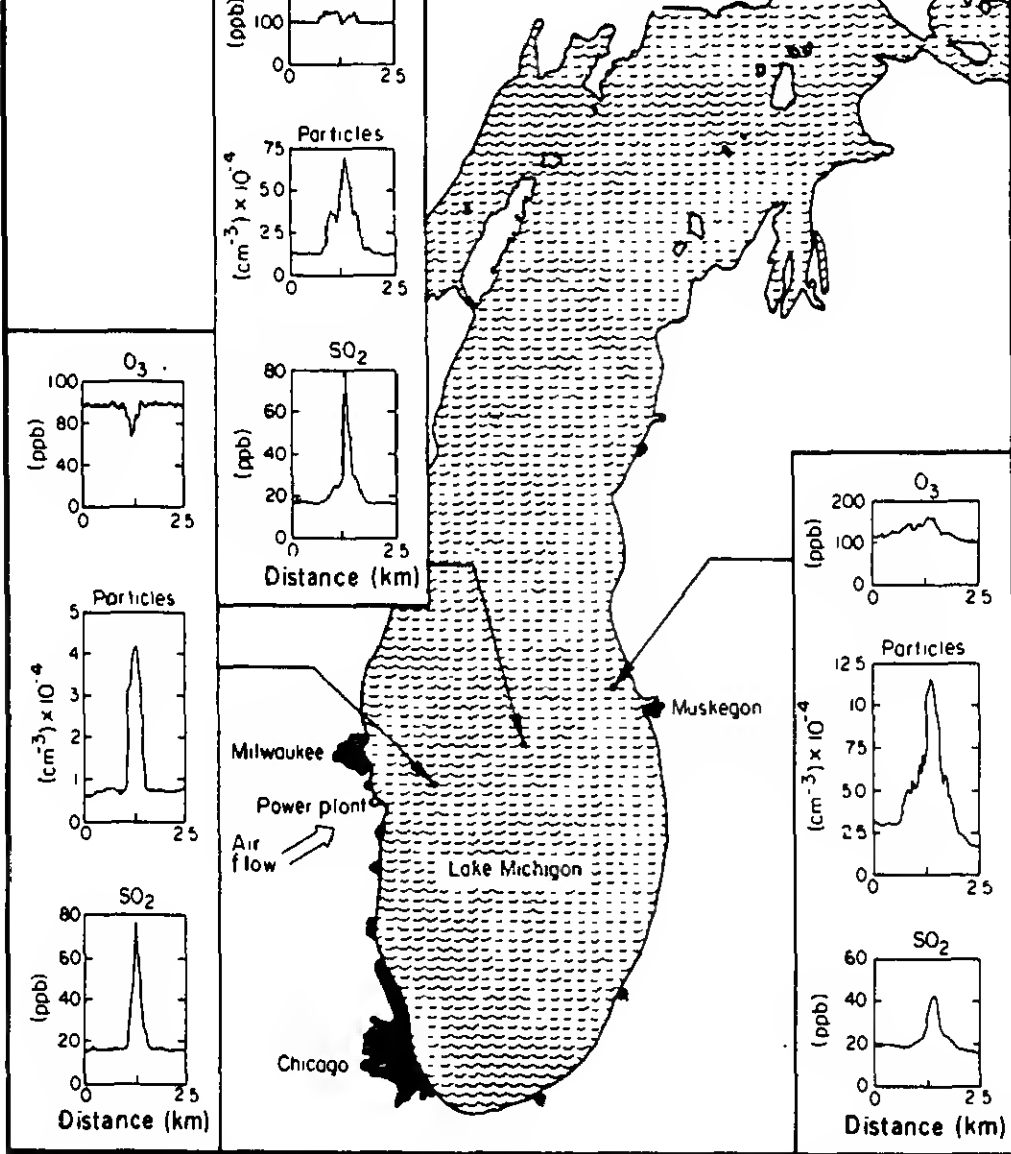
FIGURE 8.9 Aerometric data showing the concentrations of SO_2, particles larger than 0.01 μm, and O_3 in a power plant plume traveling 300 m above Lake Michigan.

8.2.4 Summary

The results of extensive power plant plume studies now indicate that

indicate that the 1-2% of the sulfur dioxide converted to sulfate during combustion and emission increases at most to 2–3% during the first 3 or 4 hours after emission, indicating, considering the experimental errors of the measurements, oxidation rates of $\leq 1\%$ per hour. Measurements during nighttime conditions have not been made in sufficient detail to ascertain whether the same low rates prevail. Data obtained when convective mixing is strong indicate significantly higher oxidation rates (reaching up to 5%/hr) suggestive of either photochemical conversion processes or possibly simply the effect of mixing the SO_2 with reactive ambient particulate matter. Due to the extensive dilution that occurs under these conditions, it has been difficult to obtain precise data and more experiments are needed to obtain firm numbers for the oxidation rate and the relative importance of photochemical and heterogeneous mechanisms.

8.3 TRANSFORMATION IN INDUSTRIAL PLUMES

Although power plants emit about two-thirds of the sulfur oxides in the eastern United States, there are a number of other major categories of sources. Of particular concern is the possible emission of S(IV) compounds.[*] To evaluate this problem, aerosol sulfur chemistry has been studied in the plumes of a copper smelter and a steel mill and contrasted with the plume of a coal-fired power plant in the arid western United States to allow evaluation of isolated sources rather than as part of an urban milieu. The presence and stability of S(IV) compounds in collected particulate samples, the conversion of SO_2 to $SO_4^{=}$, and the possible role S(IV) species may play in this conversion have been studied. An important objective of this effort has been to examine the apparent kinetics of the following reactions in particulate samples.

$$S(IV) \xrightarrow{\quad O_2 \quad} SO_4^{=} \tag{1}$$

$$S^{=} \xrightarrow{\quad O_2 \quad} S(IV) \tag{2}$$

$$SO_2(g) \rightleftharpoons S(IV) \tag{3}$$

Extensive studies on stored samples of particulate matter collected from the flue lines of copper and lead smelters and the plume of a coal fired station indicated reactions (1) and (2) are extremely slow, with time

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[*]That is, sulfur in the plus four oxidation state. In this state sulfur is considerably more reactive than in the more usual plus six oxidation

report and is shown to be reliable and rapid vis the inorganic S(IV) species.

8.3.1 Copper Smelters

Sulfur transformation chemistry was studied in the plume of the Garfield smelter in Utah from April to October 1977. A series of sampling stations were located on the eastern edge of the Oquirrh mountains at an elevation about 500 m above the smelter such that all stations were in the plume when northerly wind flows off the Salt Lake placed the plume along the mountain. Simultaneous samples were taken at up to four stations to a distance of from 4 km to 60 km from the stacks. Data were collected at each station on SO_2 concentration, lo-vol collected total particulate matter, hi-vol collected size fractionated particulate matter, wind velocity and direction, temperature, and relative humidity. Background data were collected under meteorological conditions where the plume lay to the west of the mountains or north across the lake. The complete data set has been analyzed and a detailed report is now being written. The following observations may be made about the results.

Collected particulate samples were analyzed for S(IV), sulfate, strong acid, anions, and elemental concentration using calorimetric, ion chromatographic, PIXE, ESCA and SEM-EDAX techniques. Concentrations of As and Mo in collected particulate matter were used as conservative plume tracers. It was found that the ratios Mo/As, Pb/As, and Zn/As were constant in particulate matter collected at all sampling sites for any particle size. Arsenic may thus be used as a conservative tracer of the plume. Strong mineral acid was largely neutralized within 40 km of the smelter, apparently by background metal oxide and/or carbonate particulate matter. The data indicate this neutralization process is limited only by the incorporation of basic material into the plume. S(IV) species were stable in collected particulate matter only in the neutralized material, but with proper sampling techniques could be demonstrated to be present even in very acidic particles at high ambient SO_2 concentrations. Two distinct metal – S(IV) species similar to those observed in laboratory aerosol experiments were found (Hilton et al., 1979). Formation of inorganic S(IV) species in the plume occurs, as is illustrated in Fig. 8.10. The formation of S(IV) species involves the interaction of $SO_2(g)$ with both ambient and plume derived aerosol and is equilibrium controlled. The extent of S(IV) formation is directly proportional to the $SO_2(g)$ and particulate Cu + Fe concentrations and inversely proportional to the particulate acidity.

The formation of particulate sulfate from $SO_2(g)$ also is significant as is also illustrated in Fig. 8.10. The particulate sulfate has been
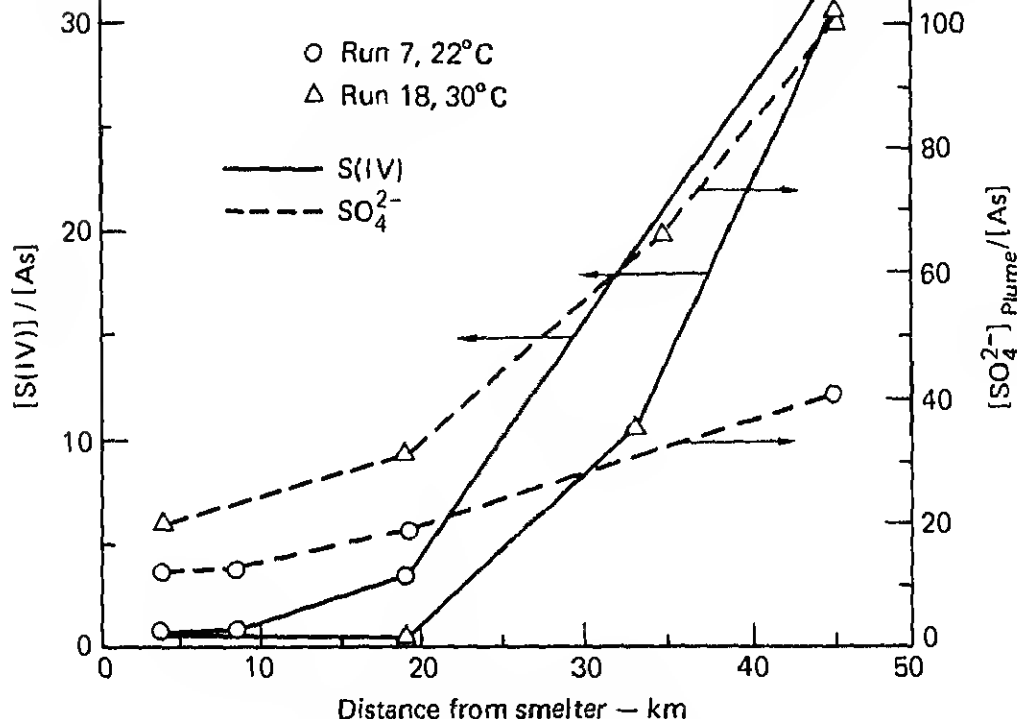
FIGURE 8.10 Plot of S(IV) or $SO_4^=$ as As ratio in 3.0 μm particulate matter as a function of distance from the smelter.

Ti as tracers for the ambient particulates. The $SO_4^=$ data thus refer to sulfate from primary smelter emissions or secondary SO_2 conversion only. Equations have been derived describing sulfur chemistry when both S(IV) and sulfate formation occur in a plume. Tests of the $SO_2(g)$ - $SO_4^=$ formation mechanisms indicate the conversion process may be described by a mechanism which is first order in $SO_2(g)$, as illustrated in Fig. 8.11. The formation of sulfate in this plume thus appears to be independent of expansion of the plume and results primarily in the formation of <0.5 μm particulate sulfate. The formation process may not be correlated with the particulate acidity, metal content, or S(IV) species. The formation of $SO_4^=$ in the plume was clearly temperature dependent. A plot of ln k_1 vs. 1/T in Fig. 8.12, gives a calculated apparent activation energy of 18.1 ± 1.3 kcal/mol.

Some work has also been done on sulfur chemistry in the Sudbury smelter plume by both the BYU and BNL groups. Analysis of aircraft collected particulate samples supplied by Environment Canada indicates

Upper plot: Linear fit if 2nd order. Vertical axis: $1/f$ (values 1.00, 1.05, 1.10, 1.15). Horizontal axis: ln t (values -0.5, 0.00, 0.5, 1.0, 1.5, 2.0).

Lower plot: O Run 7, △ Run 18. Linear fit if 1st order. Vertical axis: -ln f (values 0.00, 0.05, 0.10, 0.15, 0.20). Horizontal axis: t - hr (values 0, 1, 2, 3, 4, 5).
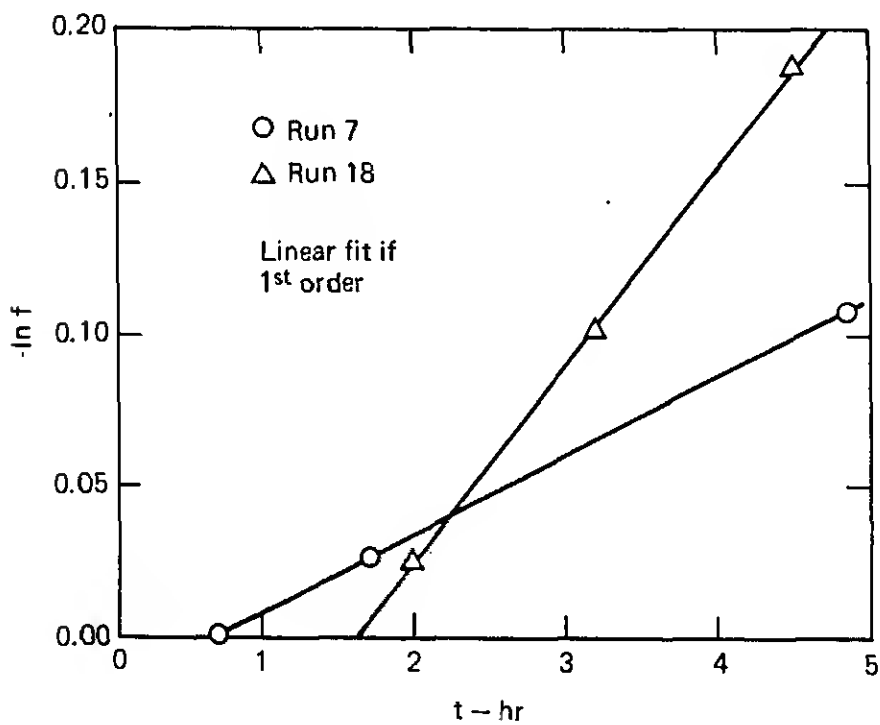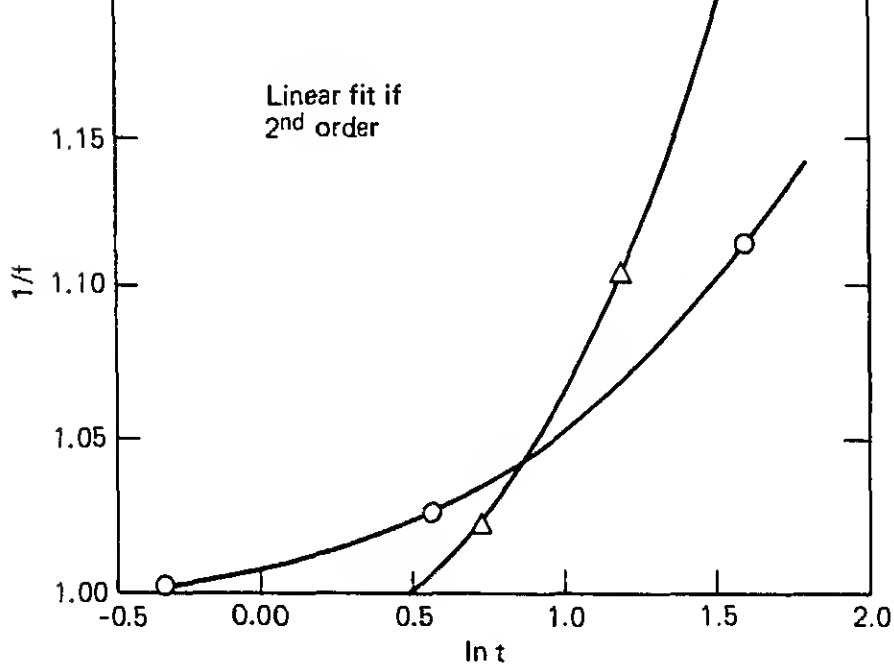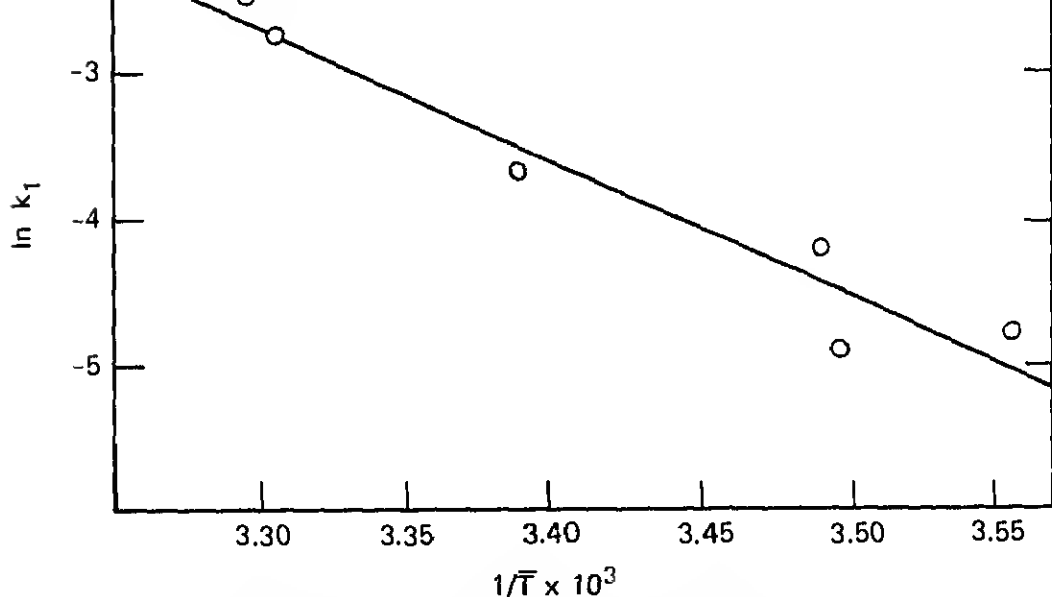
FIGURE 8.12 Arrhenius plot for the 1st order conversion of $SO_2(g)$ to $SO_4^=$ in a copper smelter plume.

the high acidity in the samples. Plume data previously reported by Lusis and Wiebe (1976) have been reinterpreted by the BNL group (Forrest, 1977b and Newman, 1977b). Lusis and Wiebe had interpreted the data in terms of a constant oxidation rate. The rate they report is slightly lower than that determined in the smelter study in Utah. The interpretation of Forrest and Newman suggests that the data are also consistent with a heterogeneous catalytic pseudo-second order mechanism. The rate of reaction was found to be 0.2 $ppm^{-1}h^{-1}$. This value is 1/5 that found for the pseudo-second order constant at an oil-fired plume. Of significance to a heterogeneous mechanism was that the emitted particulate loading of 0.04 grams per liter of emitted sulfur dioxide at the smelter operation was lower but possibly only coincidentally exactly equal to 1/5 that of the oil-fired operation.

8.3.2 Steel Mill

Sulfur transformation chemistry was studied in the plume of a steel mill from October 1977 to March 1978, using the same equipment and analytical procedures as summarized in 8.3.1. Samples from that study have been analyzed with the exception of the metal data. Some preliminary observations may be drawn from the results. The S(IV) chemistry from this source is dominated by the formation of organic-SO_2

chemistry occurring in this plume can be made using F^- as a conservative tracer, giving the results summarized in Table 8.1. This summary suggests no or little change in either S(IV) or NO_3^- content of the aerosol occur during plume transport. The increase in $SO_4^=$ may be due to $SO_2(g)$ conversion, to the incorporation of ambient $SO_4^=$ into the plume, or to both factors. It should be possible to separate out these two effects when the metal analysis that will provide tracer data for both the plume and ambient particulate matter is complete.

TABLE 8.1. Ratios of S(IV), $SO_4^=$, and NO_3^- to F^- in Particulate Samples (< 3.0 μm) from a Steel Mill for Three Different Sampling Runs.

Distance from Mill, km	S(IV)/F^-	$SO_4^=$/F^-	NO_3^-/F^-
4-6	0.79 ± 0.11	4.45 ± 0.77	25.0 ± 3.0
21	0.76 ± 0.23	6.19 ± 0.54	32.2 ± 2.6

8.3.3 Future Work

Data are not yet available on the possible formation of organic S(IV) species during plume transport or on the formation kinetics of inorganic and organic S(IV) species in power plant plumes. We have shown that source specific elements may be used to study both S(IV) and $SO_4^=$ chemistry in detail in plumes. These techniques will be used in the future to study both S(IV) and $SO_4^=$ chemistry in power plant plumes as a function of temperature, relative humidity, and solar radiation.

8.4 TRANSFORMATION IN URBAN PLUMES

In addition to power plants and industry, dispersed urban areas are important sources of sulfur oxide emissions. Major studies around St. Louis (including MISTT and RAPS studies by EPA and similar DOE studies by PNL as part of METROMEX) have shown that SO_2 is converted to $SO_4^=$ at relatively high rates in these plumes. However, reported rates for SO_2 oxidation show considerable variation.

For instance, Benarie et al. (1972) found the conversion rate of SO_2 to H_2SO_4 to vary from 6 to 25% per hour, and the average of 15 measurements was 16.6% per hour. The rates were calculated from SO_2

measurements taken at two sites, with an average value of 7.1% per hour. In their calculations, they assumed a pseudo-first order rate constant and deposition velocities of 0.7 cm/sec and 0.03 cm/sec for SO_2 and sulfate, respectively. From three separate aircraft measurements of SO_2 and sulfate, made following a tetroon downwind of St. Louis, Alkezweeny and Powell (1977) and Alkezweeny (1978) estimated the rates to be 10, 14, and 9.8% per hour. The removal rates were calculated from assumed deposition velocities of 1 cm/sec for SO_2 and 0.1 cm sec for sulfate. Assuming the same deposition velocities, Alkezweeny (1977) estimated the rates to be in the range 5.3 to 32% per hour in the St. Louis plume using SO_2 half-life time values reported by Breeding et al. (1976). Their results were based on aircraft and ground measurements of SO_2 and other trace gases downwind of the city. Meszaros et al. (1977) estimated the half-life of SO_2 in the Budapest plume to be about 2 hours; their estimate is based on sulfate and sulfur dioxide data collected about 10 km south of the city. Again if we assume the top of the mixing layer at about 2 km and 0.9 cm/sec as the difference between SO_2 and sulfate deposition velocities, the oxidation rate will be about 31% per hour.

Estimates of the conversion rate of SO_2 to sulfate have also been made out to larger scales using emission data, aircraft or ground measurements, and long range air trajectory calculations. Eliassen and Saltbones (1975) estimated in the range 0.28 to 1.73% per hour, and 1.1% per hour was estimated by Prahm et al. (1976). These two studies cover a horizontal extent of about 1000 km over Europe and the British Isles. Smith and Jeffrey (1975) found the rate to depend on the relative humidity. The rate is near zero at 60% and about 2.4% per hour at 72% relative humidities. Lavery et al. (1979) also estimated the rate to be 0.73% per hour in the Ohio Valley; their estimate is based on data collected at several SURE stations. Oxidation rates of 1.0, 4.4, 0.6, and 0.7% per hour were estimated by Elshout et al. (1978) from data collected during a four day sampling in Arnhem and Amsterdam, the Netherlands. The authors indicated that the emission of SO_2 from these cities has little influence on the measuring station; considering the wind direction, the concentrations are mainly due to SO_2 emissions from the Ruhr-area in West Germany. These values are much smaller than the transformation rates found in urban plumes.

Table 8.2 summarizes the SO_2 oxidation rates determined by various investigators. The first seven values are comparable with each other; their average values are within a factor of 4. On the other hand, the last six rates are much smaller. The difference between the two groups may be attributed to pollutant transport distances. In the first group, the

6-25	16.6	Rouen, France	Benarie et al., (1972)
1.2-13.0	7.1	Los Angeles, CA	Robert and Friedlander (1975)
31	31	Budapest, Hungary	Meszaros et al. (1977)
10-14	12	St. Louis, MO	Alkezweeny and Powell (1977)
8-11.5	9.8	St. Louis, MO	Alkezweeny (1978)
5.3-32	16.4	St. Louis, MO	Breeding et al., (1976)[*]
< 4		St. Louis, MO	DaVinci; Forrest et al. (1979)
6.8	6.8	Milwaukee, WI	MAP3S; Miller et al. (1978)
0.6-4.4	1.68	Arnhem-Amsterdam, Netherlands	Elshout et al. (1978)
0.28-1.73	0.72	Western Europe	Eliassen et al. (1975)
-	1.1	Faroe Island and British Isles	Prahm et al. (1976)
-	0(60% R.H.) 3(72% R.H.)	British Isles	Smith and Jefferey (1975)
0.73	0.73	Ohio Valley	Lavery et al. (1979)

[*]Calculated from their data by Alkezweeny (1977).

by photochemical reaction, the near zero rate during night-time hours will contribute greatly to the lower overall average rate observed during the long range transport.

8.4.1 Plume Studies Over Lake Michigan

To further these investigations, PNL has been conducting summertime field experiments over Lake Michigan since 1976 to study the rates and mechanisms of secondary pollutant formation in the Chicago and Milwaukee plumes. Emphasis is placed on sulfur dioxide to sulfate conversion. The ultimate goal of this study is to provide parameterized input for use by the MAP3S modeling community.

This area was selected for plume studies because of advantages offered by the stabilizing influence of the lake, and because the area is located in the MAP3S region. During the summer months, the surface water temperature of Lake Michigan is usually well below the ambient air temperature during daylight hours. This cooling effect of the lake along with the drastic reduction in surface roughness stabilizes off-shore flow, inhibits turbulent mixing and produces nearly laminar flow. Under such conditions, dry deposition and diffusion (competing, and often confusing processes in changing sulfur oxide concentrations) become very small and can be neglected. This introduces the possibility of interpreting plume chemistry using one-dimensional kinetics formulations, a considerable mathematical simplification over typical conditions elsewhere. Finally, the large uninterrupted fetch over the lake surface introduces the possibility of plume tracking over long distances in the absence of downwind pollutant sources.

Two types of Lagrangian experiments were conducted during this study. The earlier experiments utilized four research platforms, the PNL DC-3 and Cessena 411 aircraft, and two boats. The DC-3 aircraft performed cross sections at several altitudes through the Milwaukee plume at different downwind positions. Simultaneously, the second aircraft collected aerosol samples upwind of the city. The boats were stationed on both sides of the lake. During one week, in August 1976, cooperative experiments were carried out with NASA, EPA, and the University of Michigan. The NASA group, using a third aircraft, flew a remote CO sensor, oriented downward, over Lake Michigan. Measurements of O_3, NO/NO_x and solar radiation were made by the University of Michigan at several fixed sites along the eastern shore of the lake. Air samples were captured in bags for later analysis by EPA for hydrocarbon concentrations. A schematic summary of these activities is shown in Fig. 8.13.

FIGURE 8.13 Composite: Long Range Plume Transformation Study performed by MAP3S over Lake Michigan.

and collected samples for SO_2, sulfate, and trace metal analysis. The aircraft sampling route consisted of 16 km transects perpendicular to the tetroon trajectory. These experiments were restricted to days when high pressure circulation determined the transport winds. A subsidence inversion was usually associated with the synoptic high and surface flow was generally light with a southwesterly component.

For all studies, samples for sulfate, trace metals, SO_2, nitrate, ammonium and ammonia analysis were collected onboard the DC-3 aircraft. In addition, O_3, SO_2, NO/NO_x, light scattering, particle concentration, and aircraft location (longitude, latitude) were measured in real time and recorded on magnetic tape.

The data generated during these plume studies are of particular significance in terms of pollutants and reactions characteristic of urban plume behavior. The maximum conversion rate of sulfur dioxide to sulfate calculated from the data is about 6.8% hr^{-1}. For ozone, measurements downwind of Chicago and Milwaukee indicated that ozone is being generated within the city plumes, and that the concentration is increasing with distance from the city (Fig. 8.14). This is a feature which has been reported previously for other metropolitan areas (Cleveland and Kleiner, 1975; Alkezweeny and Drewes, 1977; White et al., 1976).

Analysis of aerosol samples collected on filters during all flights in the summer of 1976 shows an interesting relationship among the chemical constituents of aerosols. For instance, a significant correlation was found between water soluble sulfate and ammonium aerosol. However, in spite of the high correlation coefficient (0.91), the molar ratio of sulfate to ammonium is approximately 0.95. Presumably the sulfate aerosol is a mixture of sulfuric acid and ammonium sulfate, a reasonable assumption for newly produced sulfate. Furthermore, sulfate was observed to correlate more strongly with ozone (correlation coefficient of 0.56) than with trace metals, which typically exhibited correlation coefficients of much less than 0.4. Similar relationships were noted for the production rates of sulfate in the plumes, which were estimated from the data using the method of Alkezweeny and Powell (1977). The August 27 and 28 data (see Table 8.3), for example, were obtained under similar meteorological circumstances and SO_2 loadings, but exhibited marked variations in sulfate production rate. August 27 was characterized by large increases of aerosol in the light scattering range with distance downwind, and a relatively large sulfate production rate of 6.8% per hour. August 28, in contrast, exhibited essentially no sulfate production and no detectable increase in light scattering
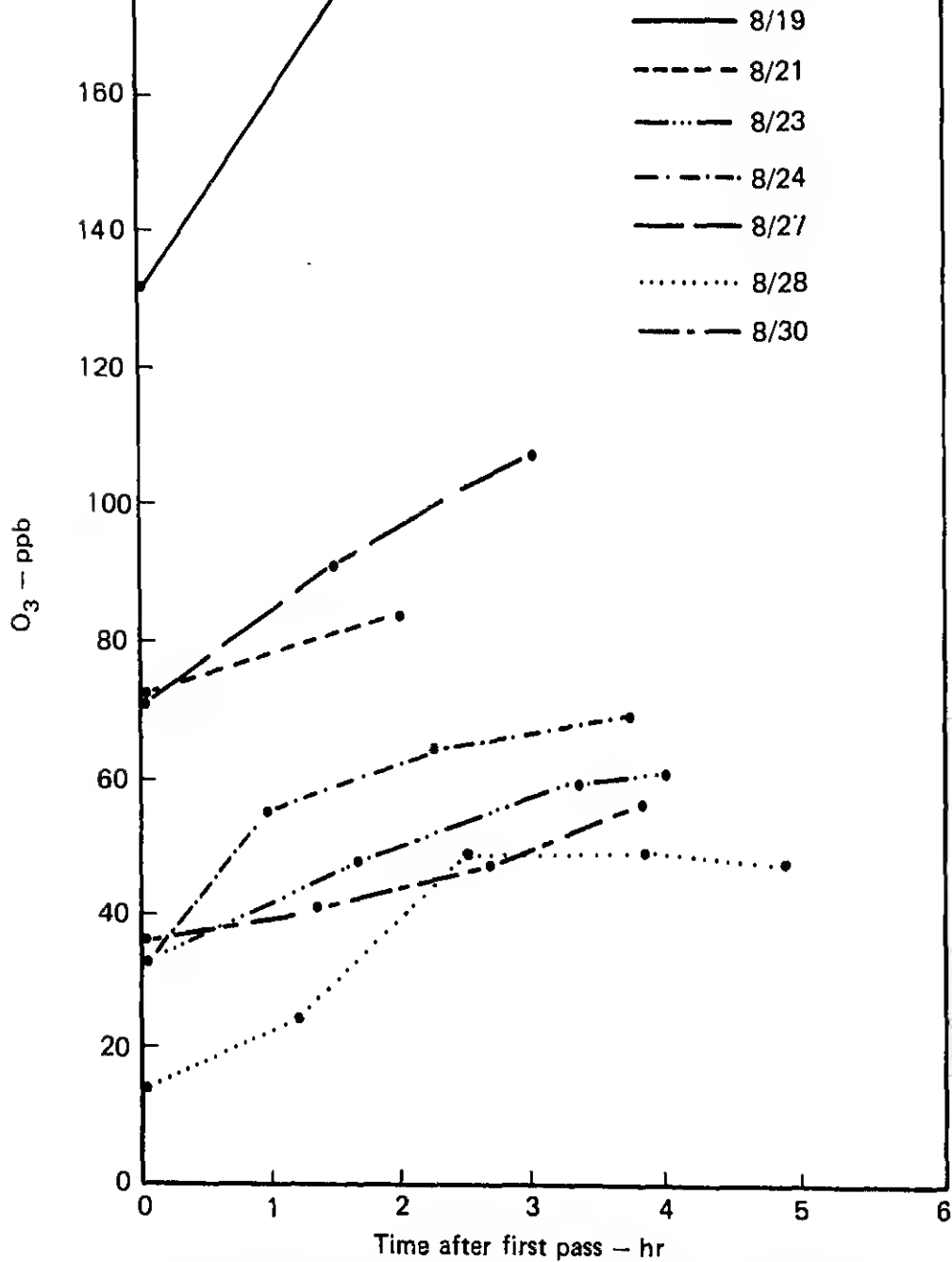
FIGURE 8.14 Results from various sampling flights in 1976 downwind of Milwaukee showing O_3 as a function of time after first.

	August 27	August 28
Upwind SO_4^- ($\mu g/m^3$)	10.6	2.2
Average SO_4^- ($\mu g/m^3$)	19.5	1.57
Average NH_4^+ ($\mu g/m^3$)	3.34	0.42
Average Pb (ng/m^3)	225.	60.
Average Ca (ng/m^3)	1700.	1820.
Average Mn (ng/m^3)	34.	96.
Average Fe (ng/m^3)	1300.	4130.
Average Zn (ng/m^3)	77.	24.
Ozone (ppb) maximum	108.	49.
Average Temperature $^{\circ}C$	28.	25.
Average R.H. %	58.	56.
k, %/hour	6.8	0
Initial SO_2, ($\mu g/m^3$)	50.	64.
Light Scattering	increased with distance	constant

The concurrent formation of sulfate and ozone noted in these experiments suggests that photochemical processes dominate the conversion of SO_2 to sulfate in urban plumes. This conclusion is also supported by the measurement of the sulfate and trace metals particle size distributions (Young and Alkezweeny, 1977); the sulfate particle size was found to be much smaller than calcium, iron, and manganese particles. The relative humidities during these experiments were less than 75%; it is possible that heterogeneous catalysis oxidation may be important at higher humidities.

The correlation between sulfate production and ozone has also been reported by other investigators. Hidy and Burton (1975) found systematic

power plant near St. Louis.

The SO_2 oxidation rates have also been determined by photochemical reaction models simulating the polluted atmosphere. Theoretical rates of 4 to 4.5% per hour were obtained by Calvert et al. (1978) and Sander and Seinfield (1976). On the other hand, Eggleton and Cox (1978) have developed a theoretical rate estimate that is between 2.2 and 6.5% per hour in urban plumes during summer months. A maximum rate of 5% per hour has been predicted by Isaken et al. (1978) to occur in the afternoon in the St. Louis plume. Their calculation of ozone build up and particulate sulfate flow rate are qualitatively in agreement with those observed by White et al. (1976).

The transformation of SO_2 to sulfate is being interpreted using a chemical kinetics code devised to simulate the photochemical reactions believed to have occurred during sampling in the urban plume. The model consisted of 53 reaction steps for irradiated SO_2-NO_x-hydrocarbons mixtures (Miller and Alkezweeny, 1979). Only three experiments have been analyzed in detail; these involved measurements within the Milwaukee plume (August 27, 1976; August 28, 1976; and July 20, 1977) as it moved eastward across the lake. Using measured NMHC levels, and conservative estimates for the rates of SO_2 reactions with free radicals, the kinetics simulation of the events predicted a maximum rate of 5% per hour. The model also predicted the observed parallel formation of O_3 and sulfate downwind of the city. According to the modeling results, OH and RO_2 were responsible for about 80% of the oxidation during the midday period while HO_2 contributed the rest. The model also simulated the interaction between urban and power plant plumes. According to the model calculation, the oxidation rate in the urban plume is higher than that in the power plant plume during the earlier stages of pollutant transport; however, at a later time and under certain conditions the situation may be reversed. It appears that when an urban air mass becomes well aged, the more reactive hydrocarbons are spent, the NO_x levels are reduced, and most of the SO_2 oxidation proceeds via the peroxy radical (HO_2, RO_2). If however there is an influx of primary pollutants, such as NO, the potential exists for regeneration of OH and for the oxidation rates of hydrocarbons and SO_2 to eventually increase. This explanation accounts for both the increased rate of SO_2 oxidation and the "ozone bulge" that were observed in the path of a power plant plume within Milwaukee's urban plume (Miller et al., 1978). Details of the model simulation have been presented by Miller and Alkezweeny (1979).

From the results of this study and others, it can be concluded that the

needed to determine the SO_2 oxidation rate at night and over long transport distances. The Lake Michigan area offers an appropriate setting for such studies because of the atmospheric stability prevailing during the summer time, and the long fetch over the lake. Because of flight time limitations, another aircraft and instrumented boats could enhance urban plume studies by increasing spatial and temporal coverage of the plume. Finally, to better understand the oxidation mechanism, the concentrations of pertinent free radicals should be determined.

8.4.2 Plume Studies Downwind of St. Louis

Simultaneous measurements of atmospheric particulate sulfate and SO_2 were made by tandem filter sampling during manned da Vinci balloon flights in 1976 (Forrest et al., 1979). The balloon permitted measurement of the evolution of chemical species while following a given air mass. On the June 8, 1976 flight the balloon encountered a relatively stagnant air mass, remaining above St. Louis County for most of the day before being carried off by nocturnal winds. Concentrations of sulfate and SO_2 remained relatively constant during an eight-hour period. Processes responsible for concentration changes were examined to set bounds upon the oxidation rate of SO_2. The data are consistent with an oxidation rate as low as zero and no greater than 4% hr^{-1}.

Samples of approximately two-hour duration were taken with a modified filter pack consisting of a quartz filter for collecting particulate sulfate followed by KOH-impregnated cellulose filters for absorbing SO_2. Both filters were analyzed by the [110]Ag tracer method. During the eight-hour period between 1200-2000 CDT that the balloon hovered over St. Louis County, SO_2 and sulfate concentrations were nearly constant. After 2000, the balloon encountered a stationary source plume and concentrations fluctuated widely.

Considering the experiment as if it were Lagrangian and assuming vertical mixing would establish a uniform vertical concentration profile up to the base of the inversion layer, any changes in SO_2 and sulfate concentrations at the balloon could be considered due to the following processes:

a. Injection of new pollutants from sources,

b. Dilution by incorporation of clean air,

c. Losses by dry deposition,

d. Chemical reaction.

reasonable assumed values of the other parameters. Increases in SO_2 and sulfate concentrations due to emissions were estimated from the output of the two stationary sources responsible for 99% of the county's emissions, and bounds placed based on zero to complete mixing in the mixing layer.

Using radiosonde potential temperature data and b_{scat} soundings, a reasonably accurate chronological account of the inversion layer height was obtained. For the eight-hour period under examination, the expansion rate averaged 0.02 h^{-1}. In the analysis, the effect of dilution by clean air caused by an increase in the inversion layer height at a rate ranging from 0 to 0.04 h^{-1} was evaluated. Deposition velocities were estimated at 1 cm sec^{-1} for SO_2 and 0.1 cm sec^{-1} for sulfate. Resulting deposition coefficients (deposition velocity/mixing height) were 0.02 h^{-1} and 0.002 h^{-1} respectively. Utilizing sulfate concentrations solely in the subsequent calculations, and assuming the sulfate deposition velocity could sometimes approach or equal that of SO_2, bounds were set for deposition losses of sulfate between 0.002 and 0.02 h^{-1}. Based upon the scatter and precision estimates for our concentration measurements, limits placed upon changes in sulfate concentration with time were set at ≤ 0.2 µg S $m^{-3}h^{-1}$.

Bounds placed on the conversion coefficient, γ, for SO_2 to sulfate oxidation were then calculated from the described estimates. For the entire rnage of parameters exmained, γ did not exceed 5.7% h^{-1}. By tightening the bounds for mixing depth increase and sulfate deposition velocity to narrower and more reasonable limits, we concluded that the oxidation rate for SO_2 to sulfate did not exceed about 4% h^{-1} in this time period, and very likely was less than 3% h^{-1}.

8.5 TRANSFORMATION ON THE REGIONAL SCALE

Although transformation has been shown to occur in the relatively high concentrations found in power plant, industrial, and urban plumes, it is the potential for continued transformation over many hours at very low concentrations that is believed ultimately to cause high region-wide sulfur particulate concentrations. Sharma and Reisinger (1978) recently reported on a box budget study conducted by TVA in 1976 that showed pollutant transformation on the regional scale. In an effort to further investigate pollutant transformation and behavior on these scales, MAP3S researchers conducted an experimental investigation of the Atmospheric Mass Balance of Industrially Emitted and Natural Sulfur (AMBIENS) in October 1977. Because it is not clear how to isolate one

Hence, the experiment became known as a "box..."

This experiment was seen as a logical extension of previous single-laboratory experiments, each of which addressed parts of the problem of pollutant transformation, transport, diffusion, and deposition that confront the MAP3S program as a whole. The specific aim of the AMBIENS experiment then became to combine previously independent investigations of pollutant behavior in order to test how well contemporary methods for formulating the above processes succeed in explaining observations.

For AMBIENS, it was proposed to attempt a pollutant box-budget study in an area similar to that defined by the grid mesh of planned regional-scale numerical models. A "box" of about 100 km x 100 km was selected as a compromise between conflicting chemical and meteorological requirements.* An early decision was made to try and simplify the experiment by locating the box in an area with very few local sources (see Fig. 8.15). By this choice, regional pollution resulting from transport over relatively long distances could be investigated rather than again studying plumes from well-identified single point sources. Southeastern Indiana was chosen as the location of the study. This area is relatively flat, has no large pollution sources, and in southwesterly flow is downwind of large sources in the lower Ohio River Valley.

The individual components that were identified as key parts of the AMBIENS experiment are listed in Table 8.4 with a further participant-task breakdown given in Table 8.5.

On meteorologically suitable occasions, aircraft from BNL and PNL sampled at different levels within the mixed layer to measure the flux of pollutants out of the Ohio River region into specially designated areas of southeastern Indiana. Several hours later, these aircraft measured the flux of pollutants in the same mass of air as it left the area. At the edges of the region, a mobile, vertically pointing correlation spectrometer (COSPEC) was also used (by EMI) to monitor the amounts of sulfur dioxide entering and leaving the AMBIENS "box" (see Fig. 8.16). As described in Section 7.1, extensive efforts were also made to characterize vertical mixing within the box.

On some occasions, meteorological changes required that the flight patterns of aircraft be adjusted as the experiment proceeded. Close contact with the National Weather Service Office in Indianapolis supplemented by numerical modeling assistance from Lawrence

_____
relatively slow transformation processes, a long time (larg... such large boxes

FIGURE 8.15 The area of the 1977 AMBIENS experiment, showing the preferred orientation of the AMBIENS "box" in southern Indiana. The main site was located near Manilla, and aircraft were operated from airports at Columbus (PNL) and Shelbyville (BNL). Crosses indicate the sites of the ANL microbarograph network.

TABLE 8.4. An Activity Breakdown of the AMBIENS Core Experiment.

AIM: To test our understanding of the behavior of atmospheric sulfur compounds over distances of the order of 100 kilometers.

Contributing Key Questions:

Chemical transformation	Aircraft (BNL, PNL)
Horizontal flux divergence	Aircraft (BNL, PNL); COSPEC (EMI)
Surface pollutant fluxes	Eddy correlation for ozone, particles (ANL); gradient methods for particulate sulfur (PNL); aerodynamic technique for SO_2 (ANL).
Planetary boundary layer structure	Lidar (SRI); Sodar (ANL); WHAT system profiles (ANL).
Micrometeorology	Normal meteorological observations, plus wind gradients and eddy fluxes of heat and momentum at main site (ANL).
Geostrophic winds	Microbarograph network (ANL).
Meteorological support	National Weather Service support (ANL); ARAC (LLL).
"Box integrity" test	Tracer experiments (BNL, ANL, LLL).
Precipitation chemistry	Wet/dry collector (ANL); Network (PNL).
Surface air chemistry	Sulfur compounds (BNL, PNL, EMI, ANL); trace metals (BNL, PNL); ozone (ANL).

Laboratory	Core Experiment Component	Peripheral Experiment
Brookhaven National Laboratory (BNL)	Aircraft monitoring Surface filter packs SF_6 tracer experiment	Trace metals
Battelle Pacific Northwest Laboratory (PNL)	Aircraft monitoring Particle fluxes	Trace metals
Argonne National Laboratory (ANL)	WHAT system profiles Sodar Geostrophic and thermal winds Micrometeorology Particle fluxes Surface sulfur Precipitation chemistry	PBL evolution Deuterated ethane Ozone fluxes
Lawrence Livermore Laboratory (LLL)	Simulation of tracer transport	Test of ARAC
SRI International (SRI)	Lidar Nephelometry	
Environmental Measurements Incorporated (EMI)	COSPEC Surface sulfur	
Naval Research Laboratory		Atmospheric conductivity

Livermore Laboratory's ARAC center and continual meteorological updating on the basis of measurements by ANL at the central site, allowed a careful watch to be maintained on evolving flow patterns. Because it was desired to test the integrity of the "box" defined by the aircraft flight patterns, some atmospheric tracer experiments were also performed (also see Sec. 7.2). The well-developed BNL capability for sulfur hexafluoride tracer work was exercised on two occasions. Tracer releases were made some 100 km upwind of the main site and samplers were set out on convenient arcs. The BNL samplers were turned on by a master command from aboard a third aircraft that carried a "sniffer" for
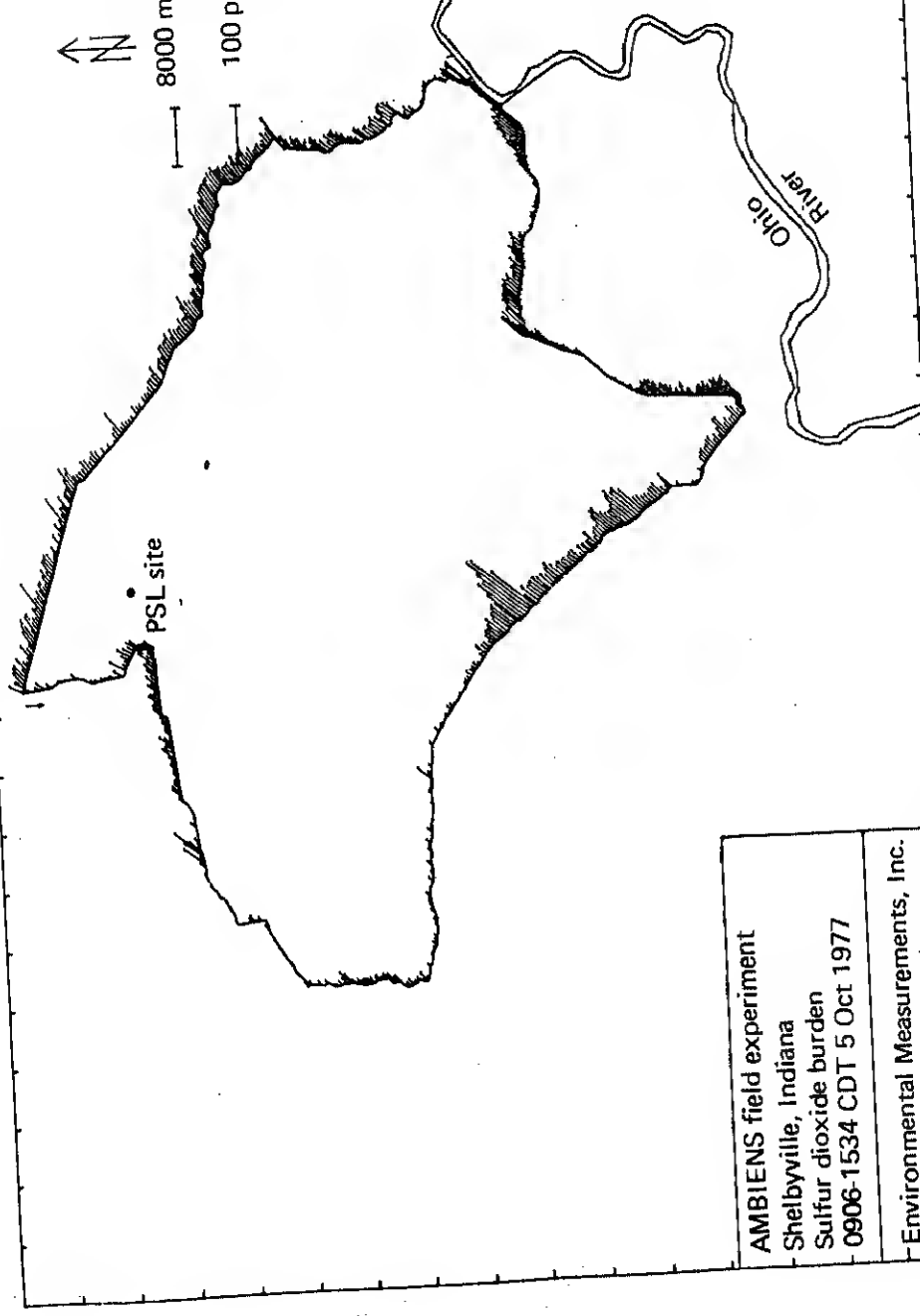
FIGURE 8.16 Results of COSPEC sampling on October 5, 1977, during MAP3S AMBIENS. The length of the short lines (going SW to NE) along the ground track of the ~indicate the total vertical burden of SO_2. A strong source is indicated upwi~ ~he Ohio River cuts across the lower right of the figure.

material (deuterated ethane, developed at ANL) was tested. Samples were collected in slowly leaking evacuated cyclinders adjacent to the BNL samplers.

The experimental plan calls for these various flux determinations to be coupled with results of chemical transformation studies and surface deposition data to derive a sulfur budget for the box. Analysis of the results from AMBIENS is now in progress. Preliminary indications are that low rates of transformation do occur, even at the low pollutant concentrations found in this relatively source free region. Further analysis and more extensive studies will be needed to confirm these results.

8.6 MODELING POLLUTANT TRANSFORMATION

A model for chemical transformation of AER pollutants is a necessary submodel within the overall modeling goal of MAP3S, and additionally is required to provide a theoretical framework to interpret results from the various field experiments examining pollutant transformation. Activity has been directed toward development of a mathematical description of the rates of chemical reactions in the sulfur oxide system, principally the oxidation of SO_2. Specifically we have examined the following processes:

- Gas-phase SO_2 oxidation in photochemically active systems, including stack plumes.

- The competition of reaction vs. dilution in expanding stack plumes in limiting SO_2 oxidation.

- The effects of diurnal variation in SO_2 oxidation rates upon residence times of SO_2 and $SO_{\overline{4}}$.

- Heterogeneous atmospheric oxidation of SO_2, i.e., in-cloud and fog water.

Ultimately transformation models must be extended to include aerosol transformations, both physical (nucleation and growth) and chemical (e.g., ammonia neutralization), but these processes have not yet been addressed in our modeling activity.

8.6.1 Gas-Phase Oxidation of SO_2
During the past few years it has become apparent that the gas-phase

free-radicals (Calvert et al., 1978). For the purpose of chemical transformations in the ambient atmosphere, one aim of the MAP3S program is to develop a region-wide atmospheric model that can incorporate transport and non-linear chemical reactions. For such application it is desirable that the chemical model be constructed with a minimum number of constituents, because the computational time and cost involved in simulating atmospheric transport with chemical transformations increase dramatically with the number of species modeled.

As a first step in constructing an atmospheric reaction mechanism suitable for incorporation into a transport model, a fairly comprehensive chemical model consisting of 44 reactions for the 30 species listed in Table 8.6 has been developed. This mechanism is based largely upon the Hecht-Seinfeld-Dodge (1974) mechanism of generalized hydrocarbon chemistry, but incorporates revised rate constant values and additional reactions. The model tests quite well against smog-chamber data for the NO_x-propylene system. Homogeneous oxidation of SO_2 is treated by including reactions with several free-radicals (HO, HO_2, RO, RO_2, $RCOO_2$) and atomic oxygen. This ATmospheric MOdel for Sulfur (ATMOS) has been used to simulate the six-hour irradiation of an $NO-NO_2-CO$-olefin mixture typical of polluted urban atmospheres (Levine and Schwartz, 1978a, 1978b). For bright sunlight (zenith angle = 40°) ATMOS predicts NO_x and ozone profiles characteristic of photochemical smog with the SO_2 oxidation rate typically 1-4% hr^{-1}. The SO_2 oxidation rate is controlled principally by reactions with HO, HO_2, and RO_2 radicals.

Using the simulation results obtained with ATMOS, we have analyzed the time-dependence of species concentrations and reaction rates and have constructed a Surrogate CHEmical MEchanism (SCHEME) that incorporates only 12 species, including NO, NO_2, O_3, olefin, and SO_2 (Levine and Schwartz, 1978b). SCHEME accurately reproduces the results of ATMOS, as indicated by the comparison in Fig. 8.17, and does so with a 5-fold decrease in execution time. SCHEME also continues to reproduce the simulation results of ATMOS even when the initial NO_x, SO_2, or olefin concentrations are changed by an order of magnitude or when the solar intensity is decreased by tenfold.

Future work on ATMOS and SCHEME will include investigations into the possibility of further reduction in the number of species required while still achieving adequate accuracy in the model predictions. Also limits should be established on the range of species concentrations or ratios of concentrations for which the assumptions and relationships used ratios of concentrations for which the assumptions and relationships used

SO_2	HO_2	H_2O	$HONO_2$	CO
NO	RO_2	O_2	HO_2NO_2	CO_2
NO_2	$RCOO_2$	O	$RONO$	SO_3
$HONO$	H_2O_2	H_2	$RONO_2$	$HOSO_2$
O_3	Olefin	NO_3	PAN	H_2SO_4
HO	Aldehyde	N_2O_5	RO	$ROSO_2$

*SCHEME employs only the species listed in the first two columns.

To gain some understanding of chemical transformations potentially important in power plant plumes and close to the stack, preliminary modeling has been carried out of the NO_x-SO_2 system in an expanding box with initial NO, NO_2, SO_2, and HONO concentrations of 500, 50, 1000, and 20 ppm, respectively. In addition, H_2O and O_2 have been initially set and fixed at constant background concentrations of 2×10^4 and 2×10^5 ppm, respectively. As anticipated, the model predicts rapid oxidation of SO_2 (maximum rate 5% hr^{-1}) at early times with a significant decrease in the oxidation rate with increasing time. Figure 8.18 shows a time profile of the percent ratio of sulfate to total sulfur predicted by this model. The primary SO_2 to sulfate mechanisms occurring in the model are the SO_2 reactions with HO and atomic oxygen. The role of this latter species is somewhat surprising in view of the competitive reaction of atomic oxygen with ambient oxygen. Further work on this model will include the use of dilution processes more sophisticated than a simple expanding box.

Modeling of transformation processes in an urban plume, including SO_2 oxidation, has been carried out by Miller and Alkezweeny (1979) as discussed in Chapter 8.4.

8.6.2 The Competition Between Dilution and SO_2 Oxidation in Expanding Stack Plumes

Early BNL stack plume studies (Newman et al., 1975; Forrest and Newman, 1977b) observed rapid early oxidation in oil-fired and smelter plumes, followed by a decrease in this rate, or apparent quenching, at increased distances from the stack. This decrease might be due either to the exhaustion of a second reagent co-emitted with SO_2, (e.g., by catalyst aoidification in the course of the oxidation reaction), or simply to dilution of these reagents with distance.
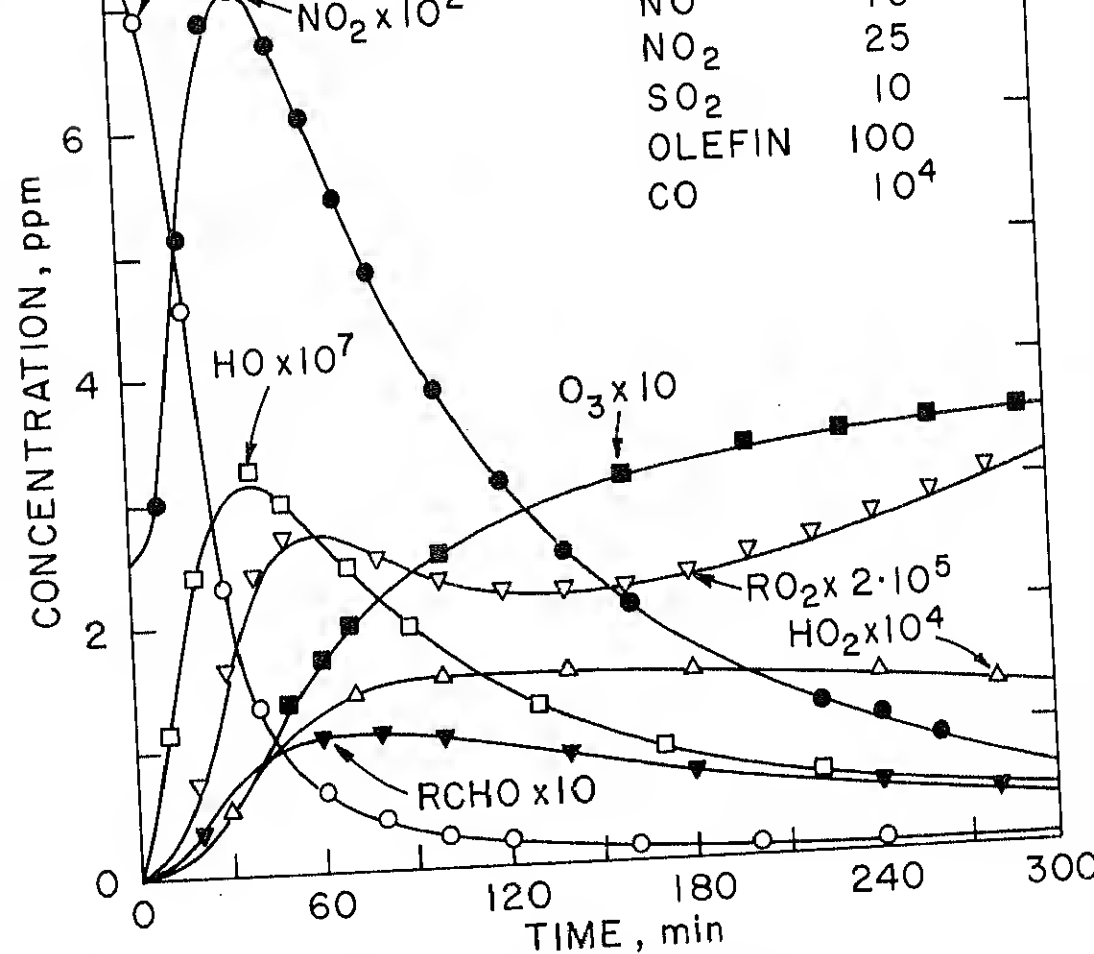
FIGURE 8.17 Comparison of simulation results using ATMOS (solid lines) and SCHEME (points) versus time of irradiation of the photochemically active mixture.

To examine the dependence of the ultimate extent of reactions in stack plumes upon this interplay between dilution and reaction, a general formalism for treating such reactions has been developed (Schwartz and Newman, 1978). This treatment was developed first for plumes of uniform cross-section and was then extended to plumes of arbitrary cross-section. It was shown that the rate of plume expansion exerts a controlling influence upon reactions that are higher than first-order in plume constituents, and that chemical reactions are quenched at high
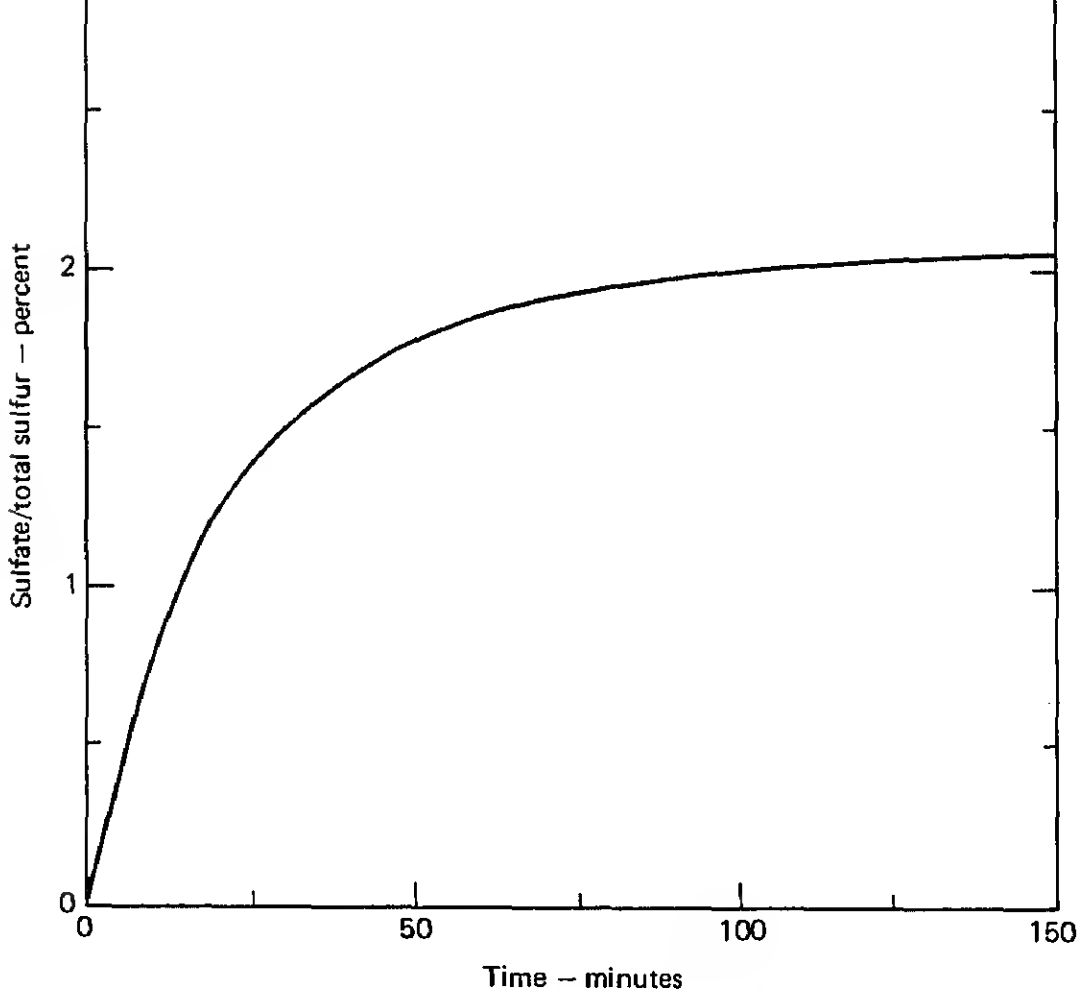
FIGURE 8.18 Simulation results for an expanding stack plume (expanding box model). Initial concentrations: SO_2 = 1000 ppm, NO = 500 ppm, NO_2 = 50 ppm, CO = 1500 ppm, and HONO = 20 ppm. All species (except O_2 and H_2O) diluted according to $dC/dt = kC$, where $k = 0.15$ min^{-1}.

expansion rates. The conditions that lead to quenching depend only upon the order of reaction and the rate of expansion and are independent of the details of the reaction mechanism. For the concentration of a conservative tracer diminishing with time proportionately to t^{-n}, a p-th order reaction is quenched for $n(p-1) > 1$ and unquenched for $n(p-1) \leq 1$. The meteorological stability classes that would lead to quenching of

This formulism was applied to a re-examination of SO_2 oxidation data obtained in studies of the Northport, NY oil-fired (Schwartz and Newman, 1978) and Sudbury, Ontario nickel-smelter plumes (Schwartz and Newman, 1977; Forrest et al., 1978) to ascertain the extent to which observed decreases in reaction rates may be ascribed either to dilution or to depletion of a catalyst or other reactive species that is co-emitted and co-diluted with SO_2. This re-examination confirmed that the mechanism of oxidation was higher than first order in plume constituents and strongly suggested second order. The data are consistent with the second-order mechanism for a wide range of assumed catalyst/SO_2 ratio. It was thus established that no inference may be drawn from such data concerning catalyst depletion as a mechanism for limiting the in-plume reaction.

8.6.3 Residence Times Under Non-Steady-State Conditions

A number of atmospheric reactions, including the oxidation of SO_2, may be expected to undergo diurnal modulation due either to increased insolation, or increased turbulent mixing during the daytime hours. The question therefore arises as to how great an influence this modulation will exert upon the residence times describing the removal of reactant and product species from the atmosphere and upon the resultant concentrations.

To address this question, the definitions of the several residence times (i.e., the mean age, the mean transit time, and the turn-over time) to encompass time-dependent rates of introduction and removal have been extended (Schwartz, 1978). This treatment led to two sets of such residence times, the first based upon the time at which the material enters the reservoir, and the second based upon the material present in the reservoir at any given observation time. The former quantities are properties only of the rates of removal processes, whereas the latter reflect also the time dependence of the rate of introduction of the material into the reservoir. Relationships were examined among the several residence times, as well as to the burden of material in the reservoir attributable to a given rate of introduction. Additionally the several definitions were extended to encompass secondary materials, i.e., materials formed in situ as a consequence of reactions of materials directly introduced.

The above framework was applied to a consideration of residence times and burdens of atmospheric SO_2 and sulfate aerosol, for assumed time-dependent rates of SO_2-to-sulfate conversion and dry deposition. It was found that even for such rates exhibiting strong diurnal modulation, as expected from considerations of photochemical reaction rates and atmospheric stability, the turn-over times and atmospheric burdens of

Regarding secondary materials, one further useful quantity is the relative burden, or the ratio of the amounts of secondary to primary materials present in the reservoir. This quantity is directly comparable to ratio of the observed concentrations of these materials and thus serves as an additional condition that must be satisfied by models describing their transformation and removal.

8.6.4 Heterogeneous Oxidation of SO_2

As a component of the MAP3S chemical modeling activity, the aqueous phase oxidation of SO_2 to sulfate in cloud or fog water has been examined. The rate of such reactions may be governed either hy the kinetics of mass transfer processes, or by reaction kinetics, depending upon the relative magnitudes of the time constants for the two processes. The time constant for diffusion in a droplet of diameter d may be approximated as

$$\tau_D = d^2/4\pi^2 D$$

where D is the diffusion coefficient for the Sulfur-IV species. The time constant for diffusion in droplets in the range of interest here is given in Table 8.7. The time constant τ_c for reaction is the inverse of the effective first-order rate coefficient k_1 for aqueous-phase oxidation,

$$k_1 = - \frac{1}{[S^{IV}]_{aq}} \cdot \frac{d[S^{IV}]_{aq}}{dt}$$

TABLE 8.7. Time constant for diffusion of S(IV) in droplets of diameter d.[*]

d(μm)	τ (sec)
1	1.4×10^{-5}
10	1.4×10^{-3}
100	1.4×10^{-1}

catalytic species such as transition metal ions (Barrie, 1976) and of the concentration of dissolved oxidants such as O_3 (Penkett et al., 1977; Larson and Harrison, 1977; Larson et al., 1978) or H_2O_2 (Penkett et al., 1977) and must be determined by laboratory measurements. However, these studies themselves are frequently not unambiguous because of difficulty in separating the kinetics of diffusion and reaction in mixed phase systems. As a part of this study, Freiberg and Schwartz (1979) have reexamined published studies of SO_2 aqueous oxidation in suspended droplets, and have found that rate coefficients for SO_2 oxidation may be substantially greater than have previously been reported. For example, for the rate coefficients computed from the data of Barrie (1976) for SO_2 oxidation in 10^{-5} to 10^{-4} M solutions of Mn^{++} and/or Fe^{++}, the error due to neglect of diffusion is as much as an order of magnitude. When the data were corrected for diffusion according to the approximate treatment developed (Freiberg and Schwartz, 1979) the effective first-order rate coefficients were found to be in the range 8×10^{-3} sec^{-1} (10^{-5} M Mn^{++}, pH = 3) to 1.3 sec^{-1} (10^{-4} M Mn^{++} + 10^{-4} M Fe^{++}, pH = 2.5). The corresponding time constants, 125 sec and 0.8 sec respectively, are long compared to the diffusional time constants given in Table 8.7, permitting the neglect of diffusion under atmospheric conditions.

If the rate coefficient k_1 is known and if it is established that the rate of oxidation is governed by the reaction kinetics rather than by mass transfer, then this rate may be computed as

$$r = 3600 \, k_1 \, L \, H_{SO_2} \, RT \gamma$$

where   r is the rate of oxidation of SO_2, hr^{-1}

   L is the liquid water content of the cloud, liter(water)/liter(air)

   H_{SO_2} is the Henry's law constant for SO_2, mol/liter atm

   R is the gas constant, lit atm/mol deg K

   T is the absolute temperature, deg K, and

   γ is the ratio of dissolved sulfur (IV) to dissolved SO_2,

$$\gamma = 1 + \frac{K_1}{+} + \frac{K_1 \, K_2}{+2}$$

Even for values of k_1 at the low end of the range given by Barrie (1976), $k_1 = 8 \times 10^{-3} \text{ sec}^{-1}$ for pH = 3, the oxidation rate for a liquid water content of 1 g/m^3 is comparable to gas phase photochemical rates, $r = 2.5\% \text{ hr}^{-1}$. Presumably this oxidation rate increases with increasing pH (due to increased solubility) and decreases with decreasing catalyst concentration, but the details of these dependences are not known.

The work described above constitutes only the beginning of the modeling activity requisite to describing heterogeneous oxidation of SO_2. Necessary future activity includes continued analysis of pertinent laboratory studies to derive appropriately parameterized values of the rate coefficient k_1, applicable to clouds and fogs of specified chemical composition. Going beyond this stage it will ultimately be necessary to develop predictive capability to describe this composition. Most important is the need to specify the pH, as influenced by the sulfur chemistry itself, by the aqueous phase chemistry of the nitrogen oxides and oxyacids, and by atmospheric ammonia, as well as carbon dioxide.

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On the global scale, concentrations of many atmospheric pollutants are essentially determined as an equilibrium between emission rates and removal processes. On the local scale, however, removal processes are often either neglected or simplified to an inordinate extent. In the case of surface removal via dry deposition, this procedure can be rationalized because of the relatively low "deposition velocities" of most contaminants of interest. Over the regional scales of interest to MAP3S, the net effect of the gross simplifications that have been popular in many early simulations remains to be tested. As an example of the extent to which the deposition process has been simplified, we might point to the common usage of 1 cm s^{-1} and 0.1 cm s^{-1} as appropriate deposition velocities for sulfur dioxide and sulfate particles, respectively, without any clear distinction as to the corresponding meteorology, terrain type, or even height of relevance. It is these matters that the MAP3S dry deposition studies have been addressing.

Earlier radioactive fallout studies showed that by far the greatest deposition to the surface was as a result of wet processes. The ratio of wet removal to dry was commonly believed to be about 10. The case of atmospheric sulfur is, however, considerably different. Fallout material usually starts from high in the atmosphere and passes through the region of major rain-related convective activity before arriving in the near vicinity of the surface where dry deposition processes are most active. However, sulfur compounds emitted into the lower troposphere are held in close contact with the surface for a considerable time, thus maximizing the opportunity for dry deposition. Current estimates seem to agree that dry and wet deposition processes deposit roughly equal quantities of sulfur, within perhaps a factor of two either way.

The field studies being undertaken as part of MAP3S follow from extensive wind-tunnel, chamber, and modeling studies conducted elsewhere. One of the major aims has been to test predictions derived from the modeling studies in order to develop some confidence in the parameterizations employed in regional-scale numerical simulations. The extent to which this process has been successful should be apparent in the following summaries of MAP3S dry deposition studies.

9.1 MEASUREMENTS OF DRY DEPOSITION

In support of efforts to include dry deposition in the modeling of pollutant behavior on a regional scale, dry deposition measurements have been performed to provide data that can be used to improve mathematical descriptions of deposition velocity, v_d, for sulfur dioxide

and these vary diurnally and seasonally in their ability to take up pollutants. The parameters most often sought in the field measurements deal with resistance, r_s, to uptake at the surface itself, rather than with the relatively well-known atmospheric properties that affect deposition in the atmospheric surface layer. To consider deposition over many different types of surfaces requires micrometeorological techniques that are both sufficiently accurate and easily deployed. Even so one can only take a rather small sample of data over surfaces representative of the major land-use types. Surface types of interest include major field crops, forests, grass, snow, bare soil, and water, to name a few. Since detailed measurements over all types of surfaces are not practical, generalization of findings to many different surface conditions is necessary. One of the purposes of the field measurements is to test and revise the hypotheses so generated.

Table 9.1 shows the major field experiments from 1976 to 1978 that were supported by MAP3S through ANL. Some of these experiments, especially those where sulfur dioxide and sulfate particles were measured directly, were also supported by the Aerosol Research Branch, ESRL, Environmental Protection Agency, Research Triangle Park, NC.

9.1.1 Research Activities

Pollutant fluxes from the atmosphere to the surface can best be measured by use of eddy-correlation techniques. The needed experiments usually require intensive efforts lasting about two weeks. To interpret the measurements, aerodynamic formulae are applied that require estimates of the eddy fluxes of momentum and heat (and sometimes water vapor) and usually of the mean values of wind speed, temperature, humidity, and concentrations of the pollutants of interest. Eddy correlation is the major technique employed because of its more likely success with the pollutant sensors available (Hicks and Wesely, 1978a). An alternative approach is the use of mean concentration gradients near the surface, but very few pollutant sensors are sufficiently stable and accurate to determine ambient concentrations to the desired accuracy of about 0.1%. Usually less difficult to meet is the demand for fast response, corresponding to an exponential time response of less than 1 s, needed for eddy-correlation measurements. As more suitable pollutant sensors are being developed, they are being considered for use in the field.

For many surfaces, the behavior of sulfur dioxide deposition is fairly well understood, even though field measurements remain sparse. For example, over vegetation the SO_2 flux appears to be controlled mostly by gaseous diffusion through stomata, much the same as the case for water

Surface	Approximate Location	Time	Fluxes Measured
grass	Wood River, IL	February 1976	particles
corn	Sangamon Co., IL	July 1976	O_3
pine forest	Alamance Co., NC	July 1977	SO_2, particles, $SO_{\bar 4}$, O_3
soybeans	Plainfield, IL	July 1977-78	O_3
senescent corn	Rush Co., IN*	October 1977	particles, O_3
snow and bare soil	Plainfield, IL	February 1978	particles, O_3
grass	Prairie View, TX	August 1978	SO_2, $SO_{\bar 4}$, particles, O_3

*This experiment was part of the AMBIENS field program.

the atmosphere by very similar mechanisms (Wesely et al., 1978), but other results (Plainfield, 1978) indicate that the similarity probably does not extend to snow or very wet surfaces where the rate of ozone uptake is very small. The average resistance to SO_2 uptake by many surfaces appears to be slightly less than $1 \, s \, cm^{-1}$, as is commonly suggested. Recent measurements at Prairie View tentatively confirm this estimate for grass. Of course, attempted generalizations cannot be carried too far. Hicks and Liss (1975) suggest that the surface resistance of lakes and oceans is very small, so that the largest resistance is usually aerodynamic. Also, resistances at very dry surfaces, or with healthy vegetation at night when stomata are closed are expected to be considerably larger than $1 \, s \, cm^{-1}$. Field experiments should be carried out to test such expectations.

ısis of the ANL deposition work concerns particles 'the size range of most of the airborne sulfate) lack of direct measurements of eddy fluxes for 1odelers have assumed that the average deposition cles at heights of 2-10 m is about $0.1 \, cm \, s^{-1}$, ar ; than that likely for gases such as sulfur dioxide.

conditions is usually much smaller ($0.05-0.5$ s cm^{-1}) due to vigorous turbulent mixing, but can become quite large in very stable conditions. The value of 0.1 cm s^{-1} for deposition velocity is usually meant to be a 24-hr average that incorporates the effects of a wide range of both aerodynamic and surface resistances. The question is not only whether 0.1 cm s^{-1} can be experimentally verified as an accurate average number, but also whether there are strong diurnal trends.

The first significant result of the field deposition work was that the flux of small particles (about 0.1 μm in diameter) to the moderately rough surface of winter grass at Wood River in 1976 was much larger than expected (Wesely et al., 1977). Surface resistance to uptake appears to be about 0.6 s cm^{-1}. However, results for particles $0.1-1.0$ μm in diameter at the pine forest of Alamance County in 1977 are not as straightforward (Wesely and Hicks, 1979). Figure 9.1 shows that at certain times particulate matter flux was directed upward. Although the deposition velocity appears large in the afternoon ($r_s < 1.5$ s cm^{-1}), the 24-hr-average magnitude is very small. A similar trend was found for the deposition velocity of total sulfur at the forest site (Hicks and Wesely, 1978b). This suggests that either biogenic sources of sulfur or resuspension of sulfur particles might be significant; future work should involve chemical measurements in plant canopies and very close to the soil surface if biogenic sources are to be considered adequately.

As shown in Fig. 9.2, a strong diurnal trend of particle flux is noted also at Rush County in the 1977 experiments above senescent corn. The lack of correlation of deposition trends with u_* (the friction velocity, which is roughly proportional to mean wind speed) indicates that resuspension is not a major factor. Another experiment, over snow and bare soil near Plainfield in 1978, indicated that particle fluxes were always directed upward, so that the removal of particles by these rather smooth surfaces is probably small and effectively countered by surface emissions.

9.1.2 Discussion

At present, the experimental work on SO_2 fluxes seems to confirm many previously held ideas about the magnitude of surface resistance to uptake and removal from the atmosphere. Deposition velocities are frequently near 1.0 cm s^{-1}. The cases of a very dry surface, such as sand, and vegetation at night need to be verified experimentally since very small deposition velocities are expected. There is an indication from the work at the pine forest in Alamance County, NC, that some surface emission of sulfur may occur at night. A future experiment at the pine forest is being considered to study this situation more
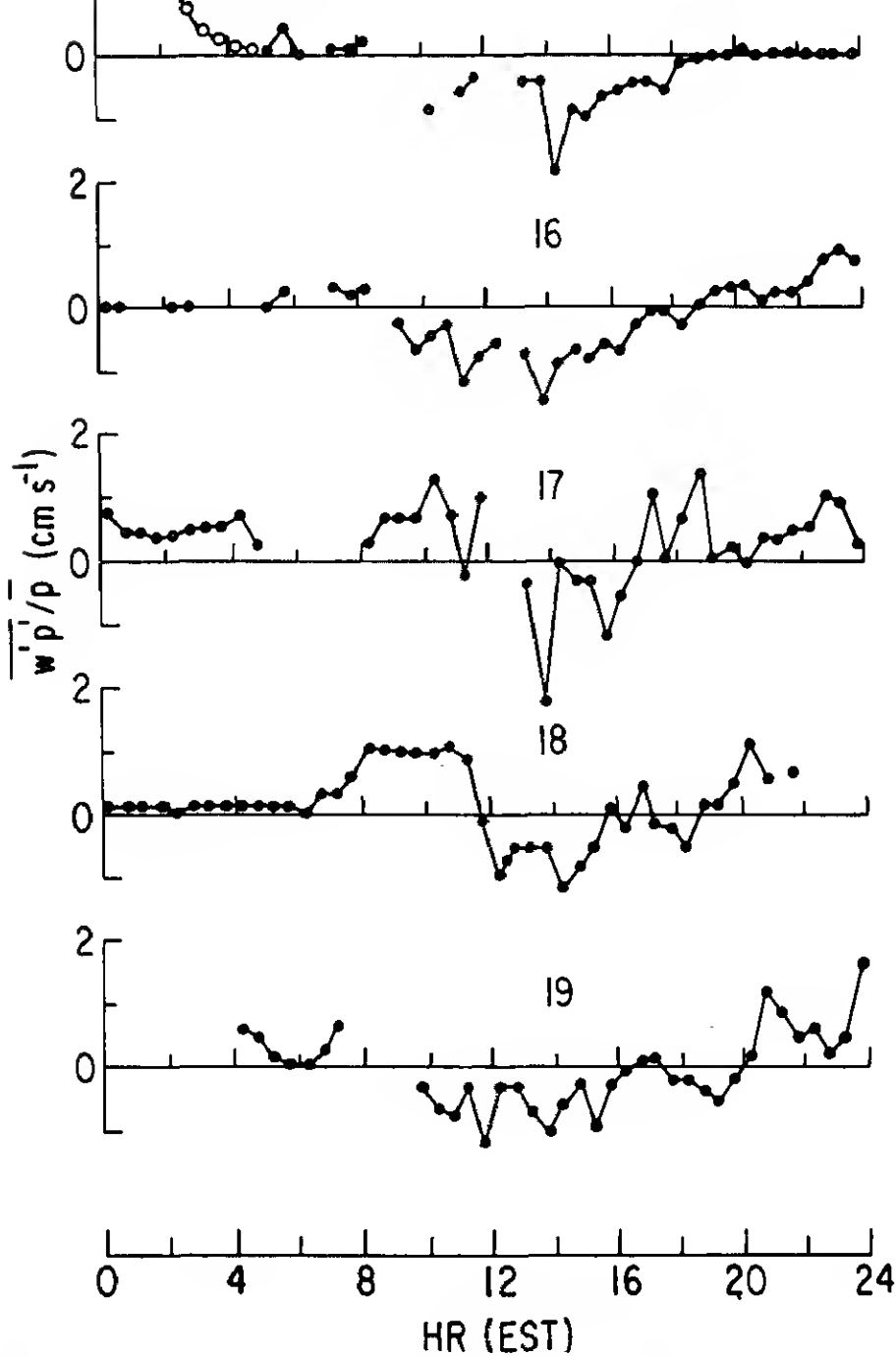
FIGURE 9.1 Vertical fluxes of particles measured above loblolly pine
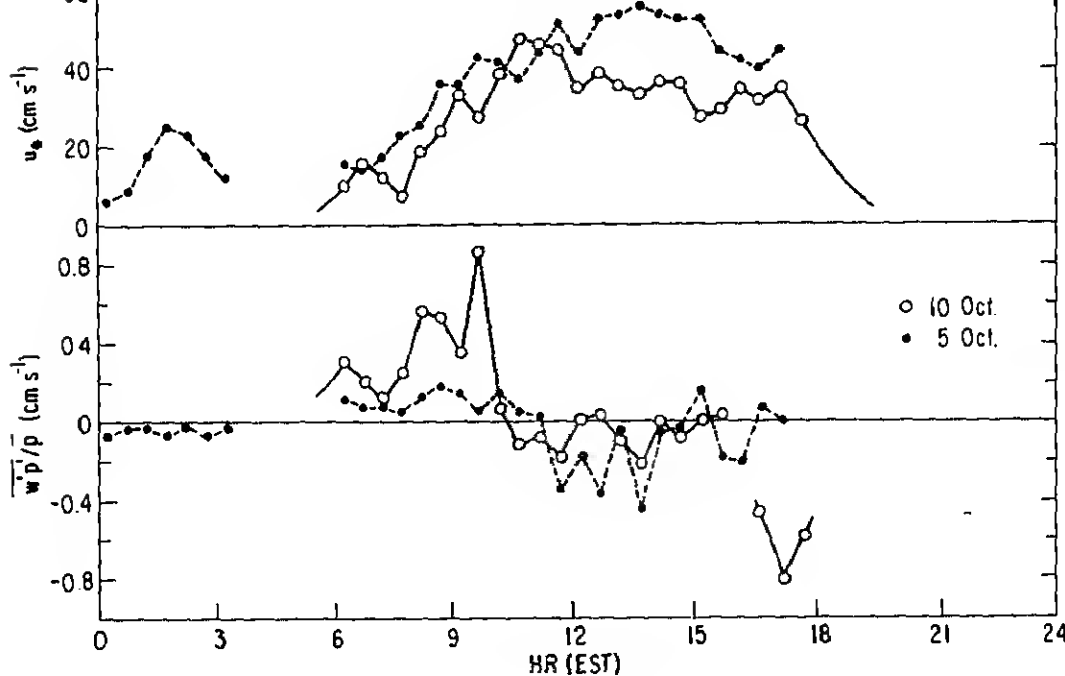
FIGURE 9.2 Particle fluxes and u_* measured during AMBIENS above senescent corn.

The best recommendation based on the field work with particle fluxes appears to be that surface resistance is near $1-2$ s cm^{-1} for many natural surfaces. Smooth surfaces such as bare soil, snow, and water seem to have much higher resistances. Surface emissions make the interpretation of these measurements difficult, especially with the particle sensor that has been used in most of the studies listed in Table 9.1. The most recent experiment, at Prairie View, should provide better information because the particle size range being sensed is better defined.

Future work will include measurement of SO_2 and SO_4^- fluxes over surfaces not yet considered. In 1979, measurement of particulate matter fluxes over Lake Michigan is planned, largely as a small addition to ongoing ecological research at ANL.

9.2 MODELING SURFACE DEPOSITION

Proper modeling of surface deposition of sulfur pollutants must be accomplished in two main parts: (1) mathematically describing the

to apply to the concentration of sulfur dioxide or particulate sulfur within the atmospheric surface layer (below 50 m) in order to obtain the vertical pollutant flux, or dry deposition. Computer simulations of pollutant transport on a regional scale often require some estimate of the v_d's to compute the loss of sulfur from the lower boundary of the volume of air considered. Most often, models reported in the literature assume constant deposition velocities of about $1.0 \cdot \mathrm{cm\,s^{-1}}$ for SO_2 and of about $0.1 \mathrm{~cm\,s^{-1}}$ for SO_4^-. In the field, however, the deposition velocity actually varies a great deal diurnally, spatially, and seasonally in the MAP3S region.

Usually, the most important (yet least well described) property that affects the deposition velocity is the resistance r_s to uptake at the surface of the earth. For example, if the surface resistance is $1 \mathrm{~s\,cm^{-1}}$, the maximum value of v_d is $1 \mathrm{~cm\,s^{-1}}$. (Inclusion of a typical amount of aerodynamic resistance will cause a decrease of v_d to near $0.8 \mathrm{~s\,cm^{-1}}$ at a height of 2-10 m.) The equations used by Sheih et al. (1979) to compute the deposition velocity in the present modeling effort are the same as those applied to determine r_s from field data.

9.2.1 Computation of Deposition Velocities

The four main parameters needed to compute deposition velocity at a certain height are surface resistance r_s, surface roughness length z_0, wind speed and some measure of atmospheric stability. If the necessary micrometeorological and surface properties are known in sufficient detail, models of pollutant behavior could include rather precise computations of the deposition velocity over surfaces in the area considered. To aid in this computation, Table 9.2 provides estimates of surface resistance for a variety of surfaces. The categories A-F indicate both the approximate state of atmospheric stability and the related ability of vegetation or other type of surface to take up SO_2, as explained more fully below. For sulfate particles, the present recommendation is that $r_s \approx 1.0 \mathrm{~s\,cm^{-1}}$, as discussed in the previous section (9.1).

In the application of many models of atmospheric transport, only rough measures of meteorological and surface parameters are available. Table 9.2 (similar results are available for each season) also provides an estimate of surface roughness, unfortunately from very limited data. The corresponding land-use types are very broad categories that apply to the eastern half of the United States, with an assumed distribution as

surface resistance to SO_2 uptake for conditions during the summer.

Land-Use Type	z_0 (cm)	r_s (s cm^{-1})			
		A,B,C	D	E	F
0, cropland and pasture	20	1.0	3.0	10.0	0.0
1, cropland, woodland and grazing land	30	1.0	3.0	10.0	0.0
2, irrigated crops	5	1.0	3.0	10.0	0.0
3, grazed forest and woodland	90	1.0	3.0	10.0	0.0
4, ungrazed forest and woodland	100	1.0	3.0	10.0	0.0
5, subhumid grassland and semiarid grazing land	10	1.0	3.0	10.0	0.0
6, open woodland grazed	20	1.0	3.0	10.0	0.0
7, desert shrubland	30	2.0	5.0	10.0	10.0
A, swamp	20	0.5	0.75	1.0	0.0
B, marshland	50	0.75	3.0	10.0	0.0
C, metropolitan city	100	10.0	10.0	10.0	0.0
F, lake or ocean	0.01	0.0	0.0	0.0	0.0

shown in Fig. 9.3. The Pasquill stability categories A-F can be estimated from such reasonably available information as wind speed and time of day. These categories have a poorly defined, but valid, relationship to the needed micrometeorological stability parameters.

The values of r_s shown in Table 9.2 are approximations subject to substantial revision as further data become available. As an example of the basis for selecting these values, it is assumed that values of $r_s = 0$ occur when the surface is wet, as when dew forms at night during non-
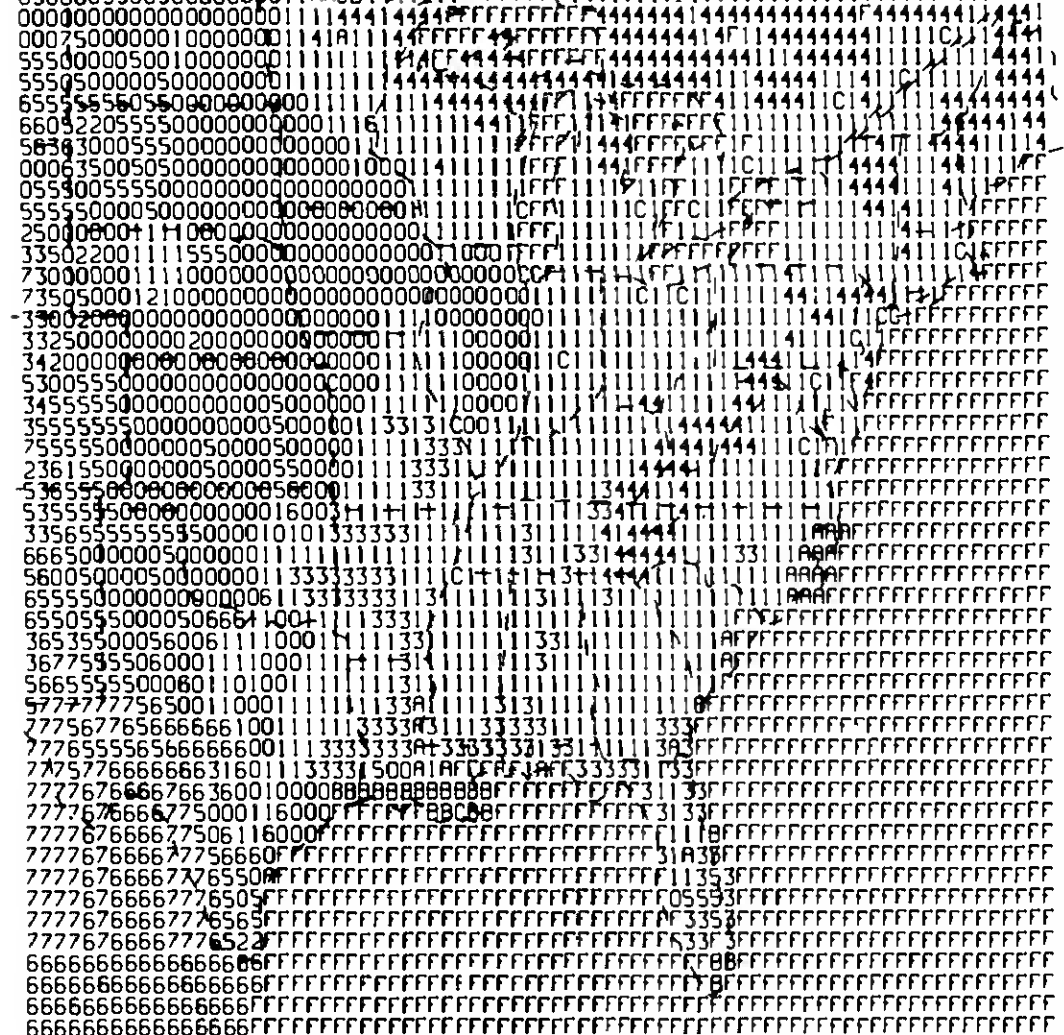
FIGURE 9.3 Land-use map represented by alphanumeric types, as listed in Table 9.2.

light winds with associated stability category F. Categories A, B, and C represent daytime conditions with solar radiation adequate to support a nearly maximum amount of photosynthesis and the concomitant vigorous uptake of gases by vegetation, resulting in a small value of r_S. Near sunrise and sunset or with very cloudy skies, r_S values in category D represent increased resistance to gas exchange by vegetation. The remaining category, E, represents nighttime conditions with moderate

surfaces with some open water exposed (land-use types A and B) have small values of r_s. As stated earlier, r_s for lakes and oceans is assumed to be zero. Finally, the rather large proportion of inert surface materials associated with urban areas should result in large values of resistance to SO_2 uptaken in the case of land-use type C.

9.2.2 Discussion

The information needed to compute sulfur dioxide and sulfate deposition velocities has been assembled for the MAP3S region and surrounding areas. The information is readily adaptable for use in numerical models describing sulfur pollution over an area within the region addressed. If meteorological data are sufficiently detailed, use of equations provided by Sheih et al. (1979) together with the estimates of z_0 and r_s can provide deposition velocities for each grid cell. On the other hand, for a Gaussian plume model that calls for only crude estimates of atmospheric conditions, the present work provides an initial set of deposition velocity maps classified according to Pasquill stability categories A to F.

The deposition maps contain no direct information on biogenic sources of sulfur released by vegetation and soils, or sulfur made airborne by sea spray. Perhaps a future step will be to derive surface source maps similar in construction to the maps of deposition velocity, so that such source terms for each grid square can be added to budget equations. At present, very little is known about biogenic sources of sulfur, especially for situations in which low rates of emission over large areas might be possible.

The surface roughnesses and resistances used in deriving deposition velocities of sulfur dioxide and sulfate particles from the basic land-use map are documented in and available from the MAP3S data bank.

Hicks, B. B. and P. S. Liss, "Transfer of SO_2 and Other Reactive Gases Across the Air-Sea Interface," Tellus, 28, 348, 1976.

Hicks, B. B. and M. L. Wesely, "An Examination of Some Micrometeorological Methods for Measuring Dry Deposition," Interagency Energy/Environment R&D Program Report, EPA-600/7-78-116, 1978a.

Hicks, B. B. and M. L. Wesely, "Recent Results for Particle Deposition Obtained by the Eddy Correlation Method," AIChE 85th National Meeting in Philadelphia, PA, 1978b.

Sheih, C. M., M. L. Wesely, and B. B. Hicks, "Estimated Dry Deposition of Sulfur Over the Eastern United States and Surrounding Regions," Atmos. Environ., in press, 1979.

Wesely, M. L., B. B. Hicks, W. P. Dannevik, S. Frisella, and R. B. Husar, "An Eddy-correlation Measurement of Particulate Deposition from the Atmosphere," Atmos. Environ., 11, 561, 1977.

Wesely, M. L., J. A. Eastman, D. R. Cook, and B. B. Hicks, "Daytime Variations of Ozone Eddy Fluxes to Maize," Boundary-Layer Meteoro., in press, 1978.

Wesely, M. L. and B. B. Hicks, "Dry Deposition and Emission of Small Particles at the Surface of the Earth," Proc. of the 4th Symposium on Turbulence, Diffusion, and Air Pollution, American Meteorological Society, Boston, in press, 1979.

Although precipitation is episodic and its spatiality is highly variable, it is an important sink for atmospheric pollutants because of the effectiveness of the wet scavenging process. In addition, the relatively high levels of pollution in the Greater Northeast have had an important effect on the chemical balance of the precipitation. Scavenging of atmospheric pollutants by precipitation includes all the processes by which pollutants are removed from the atmosphere and incorporated into rain or snow. These processes are involved in matters of much current interest, such as:

- Chemical transformations of pollutants in cloud water,

- The chemical composition of precipitation, including its acidity, and

- Deposition of pollutants and nutrients on the earth's surface by precipitation.

Precipitation scavenging of pollutants can be described best by considering in detail an example of a single species and generalizing subsequently for others. Sulfur is a logical choice for individual attention in this regard for several reasons. Being an important pollutant, it has received special emphasis during the initial stages of MAP3S, and considerable field and theoretical efforts have been expended as part of MAP3S to better understand its behavior (cf. Scott, 1978; Scott and Laulainen, 1978; Hicks, 1978; MacCracken, 1978; MAP3S, 1978; Scott and Dana, 1978; Hales, 1978; Hales and Dana, 1978a,b; Newman, 1979). Moreover, sulfur displays essentially all of the scavenging interactions that are typically important as removal processes. SO_2 can be scavenged directly as a gas, leading to the presence of dissolved SO_2 in precipitation. Sulfate, on the other hand, can be scavenged directly as an aerosol, or it can be formed in precipitation by aqueous-phase reaction of dissolved SO_2. In addition, sulfate can be formed by gas-phase SO_2 oxidation, ultimately leading to the occurrence of precipitation-borne sulfate. Although this latter process is relatively independent of wet removal, the converse is not true; indeed, gas-phase oxidation may emerge as a rate-limiting step in the overall wet removal sequence under a number of circumstances.

The above interactions are shown schematically in Fig. 10.1, where the pathways between boxes can be envisioned as focal points for MAP3S research emphasis. It is expected that roughly one-third of the MAP3S-area sulfur emissions are removed within the region by

| Gaseous sulfur compounds in air | ← Chemical reaction → | Particulate sulfur compounds in air |

Absorption / Desorption (left side)

Hydrometer evaporation / Scavenging (right side)

| Volatile sulfur compounds dissolved in hydrometeors | ← Chemical reaction → | Nonvolatile sulfur compounds in hydrometeors |

Deposition / Desorption (left side)

Deposition / Resuspension (right side)

| Volatile sulfur compounds | Chemical reaction | Nonvolatile sulfur compounds |

needed if adequate understanding is to be available for evaluating alternative control strategies.

10.1 POLLUTANT SCAVENGING IN WINTER STORMS

10.1.1 Research Activities

To help examine and predict the wet removal of pollutants from the atmosphere, an extensive sampling program has been conducted near Muskegon, Michigan, during the past two winters (1976-77, 1977-78). The sampling program has been designed to examine primarily the water and pollutant budgets of lake effect snowstorms, but all precipitation events (lake effect and/or frontal) were sampled when possible. A third year of winter time wet removal measurements are now being obtained near Muskegon.

The Muskegon site was selected because of the relatively high frequency of winter, lake-effect snow squalls. The occurrence of these storms is readily predictable, thus facilitating coordination between ground and aircraft sampling crews. In addition, the storms are of low intensity, are long lasting and are nearly stationary, all factors that enable frequent cloud penetrations and extensive sampling time in the clear air at the cloud boundaries. A particular advantage in examining these wintertime snowstorms is that the growth histories of precipitation particles can be determined from the shape of the replicated ice particles. Such information is lost when ice particles melt to form rain.

During the months of March and December 1977, and January 1978, over a dozen storm events occurred in which surface precipitation samples were collected. Supplemental aircraft observations were available during 10 of these periods. During each storm period, sequential samples of surface precipitation were obtained for chemical analysis at approximately one hour intervals at one to three sites. Additional data collected at the surface sites included meteorological observations and replicas of the falling ice crystals for determination of growth histories of the precipitation particles.

Simultaneously with the surface sampling, aircraft concentration measurements were obtained of $SO_4^=$ aerosol mass, cloud condensation nuclei, SO_2, O_3 and total ammonia. The size distribution for aerosol was also determined for sizes ranging from 0.01 μm to approximately 7 μm. These "clear air" measurements took place in the subcloud layer

Upon completion of these clear air observations, the aircraft would sample in-cloud at locations approximately upwind of the surface sampling sites. Measurements were obtained of cloud liquid water concentration and droplet size distributions. Replicas of cloud particles, and samples of the supercooled cloud water for chemical analysis were also obtained.

Figure 10.2 schematically illustrates the various sampling platforms and their orientations with respect to each other during a lake effect episode. The aircraft generally samples upwind over the lake and downwind from the storm before proceeding incloud for cloud microphysical measurements. Surface sampling takes place at several sites near Muskegon. Radar support comes from 2 weather radars. Supplemental meteorological data are available from a University of Chicago aircraft based at Muskegon for a NSF sponsored research program.

10.1.2 Research Results

Table 10.1 provides a survey of the aircraft observations taken during the past two years. Cloud liquid water concentrations during December 1977, were higher than in March 1977, and January 1978, when only two flights detected measurable cloud droplet water. The sulfate and nitrate concentrations generally ranged between two and ten times the concentrations found in the surface water samples; suggesting that the cloud liquid water was removed by large, clean, collector particles (snowflakes). Subcloud sulfate air concentrations were typically around $3 \ \mu g/m^3$ with extreme values of 0.7 and 9.5 $\mu g/m^3$. Between 50% and 90% of the subcloud sulfate appears to have been activated as cloud condensation nuclei in the storms.

Surface samples of sulfate and nitrate concentrations were found to vary by a factor of two or more between sites on any given day, and varied by a factor of ten or more from storm to storm. The highest sulfate concentration observed in surface precipitation was 10 mg/l on March 5, 1977, while the smallest value was 0.2 mg/l on December 10, 1977.

Comparisons of concentrations on different days illustrates that when nitrate concentrations are high, sulfate concentrations are either high or low. However, when nitrate concentrations are low, sulfate concentrations are also low. Such variability suggests that either the removal mechanisms are substantially different for sulfate and nitrate, or that the vertical distributions (i.e., the source regions) for each pollutant are substantially different.
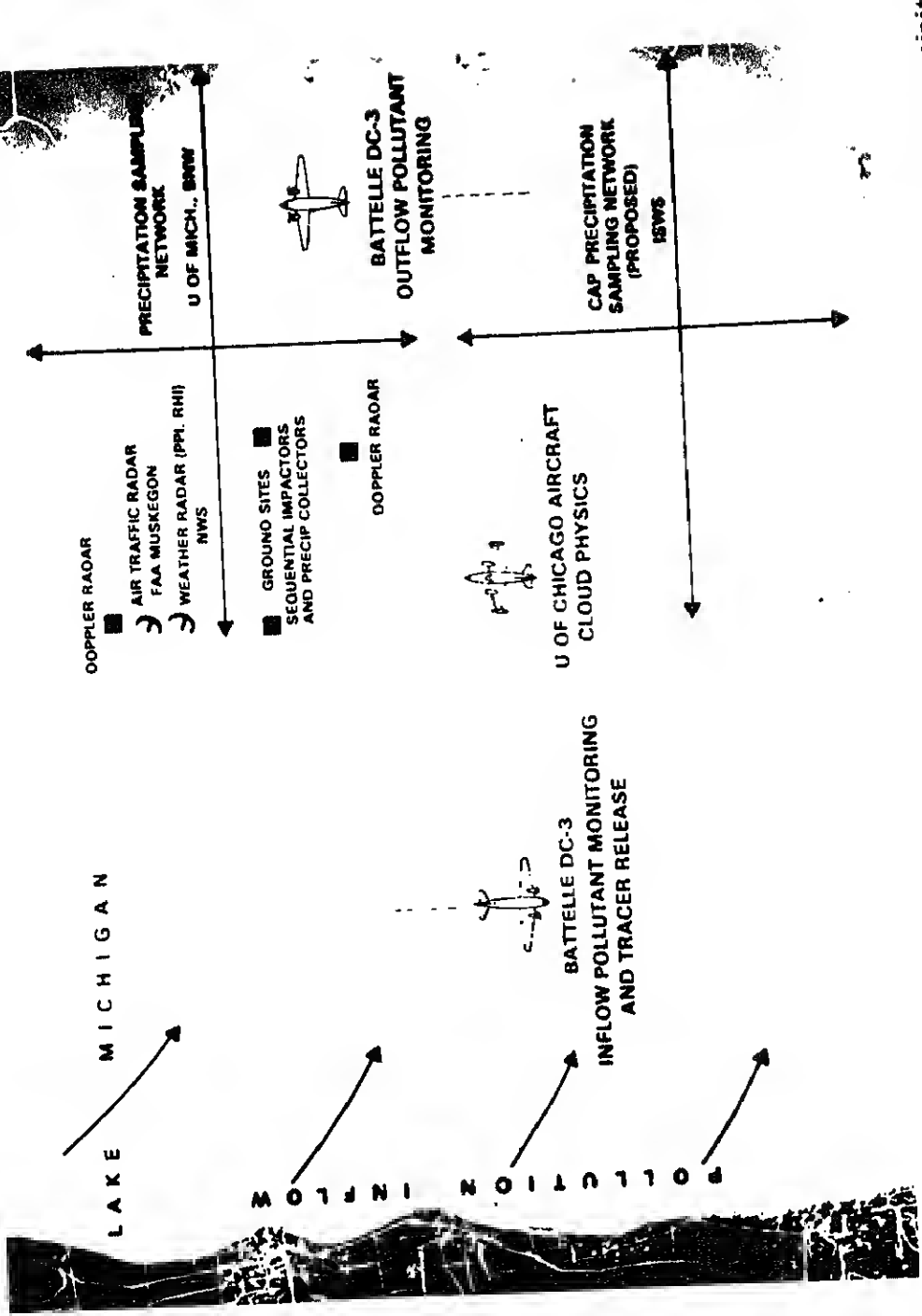
FIGURE 10.2 Schematic illustrating various sampling platforms utilized during Muskegon precipitation experiments.

Date	In-Cloud Altitude (m-msl)	Cloud Water g/m³	Water $SO_4^=$ (mg/l)	Water NO_3^- (mg/l)	Cloud $SO_4^=$ (µg/m³)	Fraction $SO_4^=$ Activated
12/2/77	1525 1220	0.18 0.11	9.8 11.7	5.4 8.3	2.6	0.50-0.85
12/6/77	915	0.28	9.3	8.2	N/A	N/A
12/7/77	1220	0.14	6.5	6.0	1.4	0.55-0.85
12/10/77	915	0.09	6.6	3.0	0.7	0.82-0.88
1/25/78	600-1525	0	N/A	N/A	9.5	N/A
1/30/78	760-915	0.02-0.04	N/A	N/A	2.7	N/A
1/31/78	1065	0.04-0.06	29.8	49.5	2.4	0.50-0.65
2/1/78	670-915	0.00-0.03	N/A	N/A	2.8	N/A
3/5/77	670 1525	0.10 0.16	32.9 12.0	29.6 10.2	5.9	0.55-0.65
3/17/77	1525-1700	0	N/A	N/A	2.4	N/A

N/A = Not Available

Values of pH for individual surface samples ranged between 3.78 and 7.09 with the average pH over all storms being near 4.5. It appears that those samples that contained less acidic precipitation consistently contained high concentrations of K, Mg, and Ca. Thus, the wind-blown, alkaline soil from shoreline dunes near Lake Michigan and from exposed ground appears to have contributed to the anomalously high pH values (as compared to expected clean water values of pH ∿5.6).

It is also of interest to note that comparisons of pH with nitrate and sulfate concentrations in sequential samples suggest that the fluctuations in pH were more highly correlated with the fluctuations in the nitrate concentrations than with the sulfate fluctuations.

illustrates the presence of two such bands that contributed to increases in pollutant concentration in surface precipitation samples. Table 10.2 presents the chemical variability of precipitation during passage of the above mentioned bands. The most striking relationship in Table 10.2 is the correspondence between enhanced wet-removal and the passage of these bands of precipitation (see "comments" section of Table 10.2). The greater radar returns from these bands suggest more intense precipitation and a strong likelihood of significant cloud liquid water concentration. The simultaneous increase in the concentration of all the materials listed in Table 10.2 during the band passages suggests enhanced below cloud removal associated with larger collector particles and greater precipitation rates. In addition, the higher concentrations of pollutant in the snow associated with the bands may have resulted from enhanced mesoscale conversion in the vicinity of the bands. That is, the bands probably processed more polluted air per unit time than the surrounding clouds. However, with the exception of sodium, sulfate appears to be removed somewhat more efficiently than the other materials during the band passages.

10.1.3 Discussion

In every winter storm event encountered to date, there has been sufficient pre-existing sulfate to account for the observed sulfate concentrations in precipitation. The existing, sub-cloud sulfate appears to act as droplet nuclei. These nucleated droplets then appear to be effectively accreted by large snowflakes falling from above.

Figure 10.4 presents data that help to substantiate the above claim. Individual precipitation samples are plotted and compared with the theoretical predictions (solid line) arising from analysis of the Muskegon field data taken during the first winter sampling period. The open circles represent surface precipitation data collected on days during which no liquid water was detected in the clouds, or during which little or no riming was detected on the ice particles at the surface. The solid circles represent surface precipitation data collected on days with detectable cloud water or when the majority of the replicated ice particles were rimed. That is, the solid circle data represent events when precipitation particles were growing mainly to accreting cloud droplets (riming), while the open circle data indicate particle growth primarily by vapor deposition onto existing ice crystals. The greatest sulfate washout occurs when the precipitation particles are growing by riming. Thus, the washout ratio data are highly suggestive that the sulfate nucleation-riming mechanism, postulated from previous studies (Scott and Laulainen, 1978), is the predominant sulfur removal mechanism in these wintertime snowstorms. In-cloud conversion of SO_2 to SO_4 does
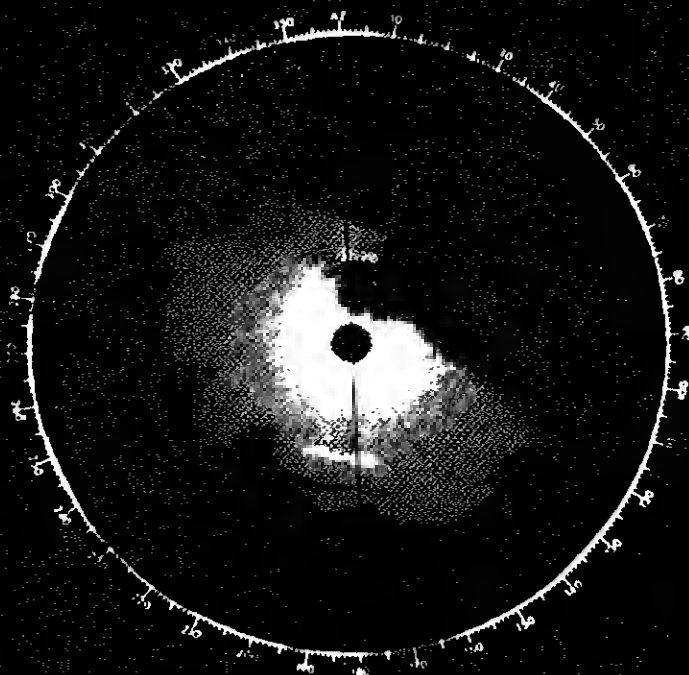
	Sample				
	B1	B2	B3	B4	B5
Time	1915-1953	1940-2016	2000-2037	2025-2100	2045-211
Muskegon Temp.	4°C		2°C		1°C
pH	6.8	6.7	6.3	6.3	5.8
$SO_4^=$ mg/l	1.2	0.8	0.6	1.6	4.3
NO_3^- mg/l	2.5	1.3	1.2	1.9	2.9
Cl^- mg/l	0.4	0.3	0.2	0.3	0.5
NH_4^+ mg/l	0.6	0.3	0.3	0.5	0.5
Na^+ mg/l	0.4	0.1	0.1	0.4	1.0
K^+ mg/l	6.3	-	0.1	0.5	0.1
Ca^{++} mg/l	1.7	0.9	0.6	1.0	1.8
Mg^{++} mg/l	0.5	0.2	0.2	0.3	0.6
Comments	band passage	-	-	band arrives 2045	band arrives 2045

Wet removal, being a major sink of atmospheric sulfur, is a important component of models predicting sulfate concentrations ov large scales and time intervals. Once effective removal a transformation mechanisms have been established, rates of removir atmospheric pollutants and locations of removal may be able to l predicted on an event-to-event basis. The bulk of the data collected far have been valuable for the formation of hypotheses about w removal of pollutants. The increasing data set has also been essential f testing parameterizations of wet removal developed during the course
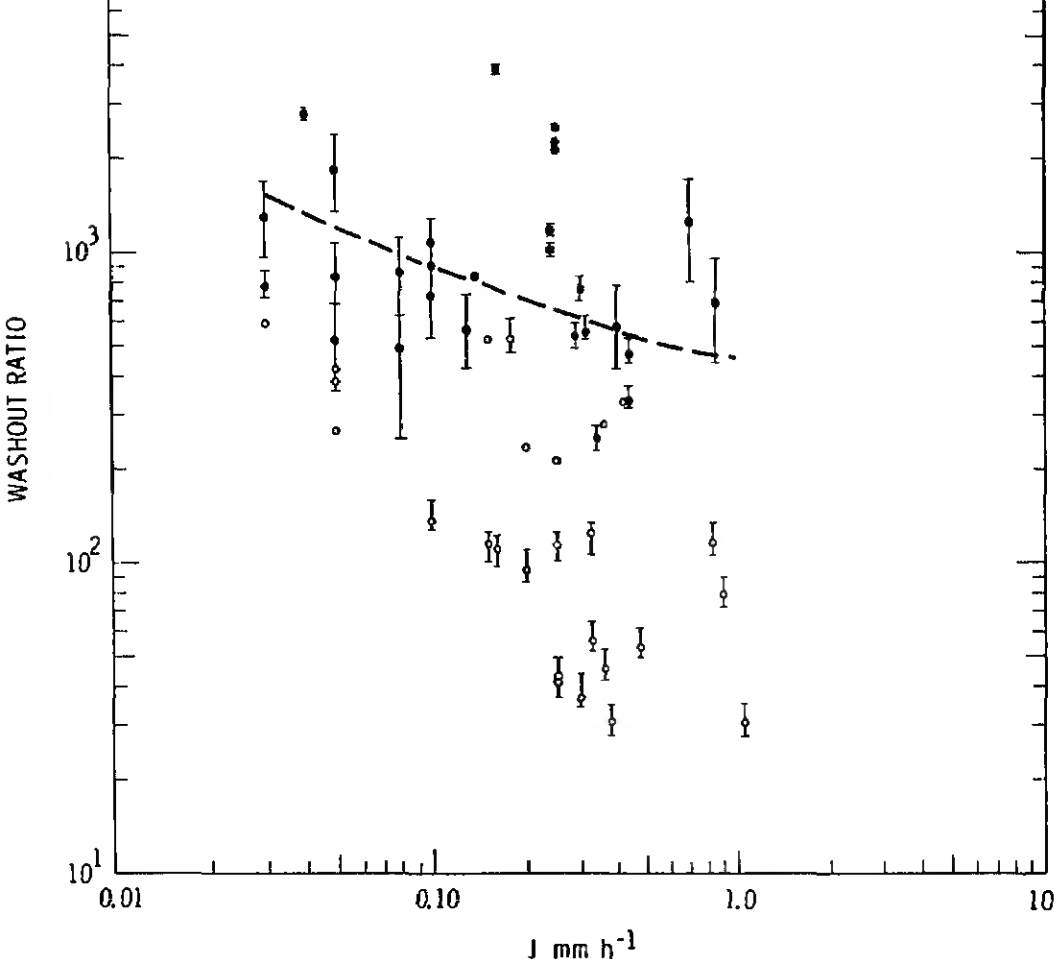
FIGURE 10.4 Sulfate washout ratio as a function of precipitation rate (J) for rimed (●) and unrimed (o) snow.

10.2 POLLUTANT SCAVENGING IN SUMMER CONVECTIVE STORMS

10.2.1 Research Activities

Scavenging of pollutants by summer convective storms is important because such storms account for a major portion of annual rainfall in most areas of the eastern United States, and because the highest precipitation acidities (lowest pH values) in this region have been observed during the summer.

Recent research on this subject sponsored by MAP3S includes:

(ISWS) and Battelle Pacific Northwest Laboratories (PNL).

- Weekly sampling of aerosols at MAP3S precipitation sampling sites to provide data for calculating the scavenging ratio of pollutant concentrations in rain to those in air (see Section 6.1).

- Development of methods for identifying the sources of pollutants in both aerosol and precipitation samples.

- Field experiments in rural Illinois to investigate sulfur scavenging in individual convective cells.

Additional details and current results of this research are presented in the following sections.

10.2.2 Research Results

10.2.2.1 St. Louis METROMEX Results

Research groups from both ISWS and PNL were active in project METROMEX (METROpolitan Meteorological Experiment) at St. Louis, 1971-1975 (Changnon et al., 1971). Both groups operated networks of samplers to collect precipitation. Water samples were analyzed for natural and anthropogenic constituents as well as for tracer materials "injected" into convective storms.

Tracer Experiments. The two main goals of tracer experiments on precipitation systems are: (1) to trace trajectories of materials in air and attached to precipitation, and (2) to measure scavenging efficiencies (fractions of tracer deposited). A recent review of this subject (Gatz, 1977) reports results of some of the METROMEX tracer experiments carried out by PNL. Gatz (1975) gave current results of ISWS METROMEX tracer experiments. This work was arranged so that ISWS released tracer at relatively low altitudes in the updraft of warm moist air feeding a convective storm; the PNL releases were made at middle levels on the upwind side of such storms. On one occasion, both organizations released tracer into the same convective cell.

Results of these and other tracer experiments on precipitation systems show tracer deposition at locations that suggest extremely complex trajectories and exchange between convective cells (Semonin, 1972; Young et al., 1974, 1976, 1977).

Measured scavenging efficiencies range from 5% to over 100% (Gatz, 1977). Efficiencies over 100% suggest that background concentrations of

lons, both natural and anthropogenic, were measured by PNL and ISWS in sampling networks around St. Louis. These measurements were made (1) to assess deposition patterns and removal efficiencies of several constituents having urban sources, (2) to provide data on elements that might serve as predictors of background levels of tracer elements, and (3) to measure variability of deposition over relatively small areas near a large city.

Figure 10.5 shows mean patterns of deposition (each normalized by dividing individual values by the network mean) in 26 rains for K, Zn, and rainfall. It shows that a large portion of the Zn in rain is deposited in rather close proximity to its urban sources, whereas K, having a more uniformly distributed source (primarily soil dust), is quite uniformly distributed in the rain.

Scavenging ratios, W (ratios of the concentration of material in rain to that in air), have been suggested as useful in predicting deposition of airborne materials in rain (Engelman, 1971). Figure 10.6 was prepared from data on total Pb, Zn, Mn, Fe, and Mg in aerosols and precipitation collected at St. Louis. It shows that mean concentrations in rain (relative to air) increase with both particle size and distance from St. Louis. The range of values obtained by Cawse (1972) at even greater distances from local sources in the U. K. is shown for comparison. Such relationships are useful for prediction of deposition on seasonal or annual time scales.

During the past year a significant effort within MAP3S has been devoted to the interpretation of the previously unanalyzed data base pertaining to the scavenging of $SO_{\bar{4}}$, $NO_{\bar{3}}$, SO_2, $NO_{\bar{2}}$, and $NH_{\bar{4}}^+$ by convective storm systems. This data base was generated in St. Louis during the summers of 1972 and 1973 from an experiment designed to provide a material-balance inventory of storms passing across the urban area (Hales and Dana, 1979).

Results of this study indicate that SO_x and NO_x are removed rather efficiently by convective storms, and that significant amounts of these materials recovered by the network originated from local sources. Example results are shown in Fig. 10.7a-d, which indicate that $NO_{\bar{3}}$ and $SO_{\bar{4}}$ bear a definite relationship to the urban source whereas $NH_{\bar{4}}^+$ behaves more like a rurally-generated constituent. When background effects are removed from these data, the storm shown here appears to have scavenged sufficient $SO_{\bar{4}}$ and $NO_{\bar{3}}$ to account, respectively, for about 36 and 13 percent of the urban generation rate.

One possible explanation of the high SO_x removal rates is that SO_2
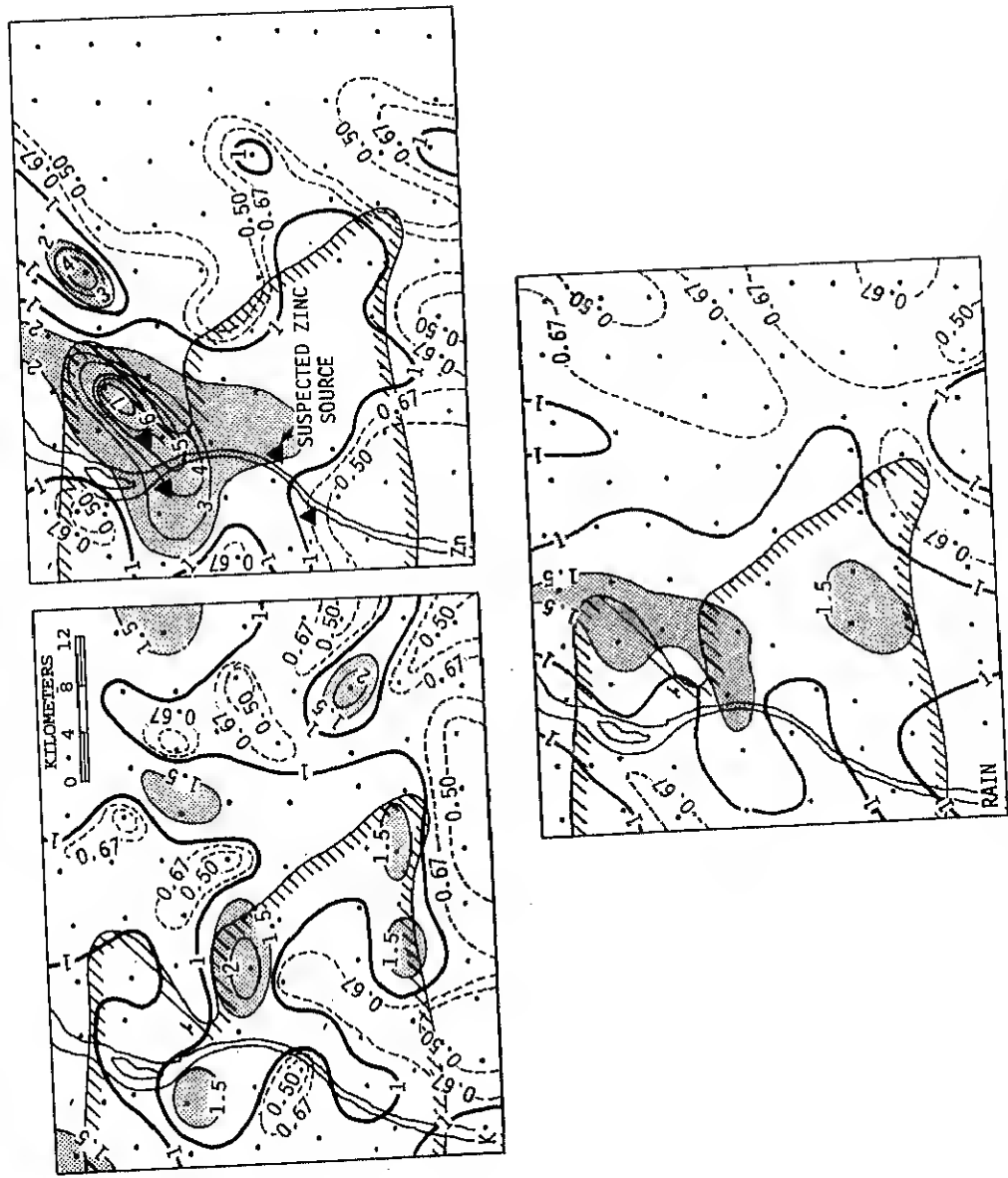
FIGURE 10.5 Deposition of K, Zn, and rainfall from 26 events in METROMEX. Units are dimensionless, being ratios of actual deposition divided by the respective network means.
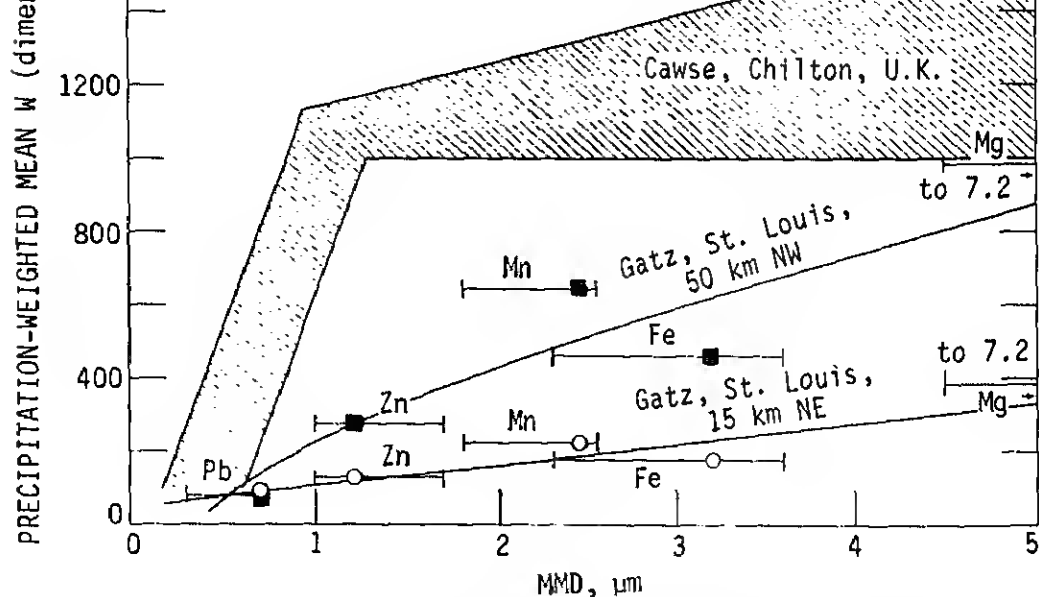
FIGURE 10.6 Variation of scavenging ratio (W) with mass median diameter (MMD) and distance from urban sources for St. Louis and Chilton, U. K.

storms where little aqueous-phase conversion was detected (Scott and Laulainen, 1978, and Section 10.1). This speculation suggests that much of the observed cycling in annual $SO_4^=$ concentrations can be explained in terms of aqueous-phase oxidation in nonprecipitating clouds, which occurs rapidly during warm summertime conditions but becomes negligible during winter months.

Relative variability of deposition for elements having widespread sources at St. Louis (Li, Na, Mg, K, and Ca) exceeds values in the literature for networks of similar size. However, this may result at least partially from the closer spacing of samplers used at St. Louis, as seen in the proportionately greater variability of St. Louis rainfall. The variability of Zn deposition at St. Louis was considerably greater than that of rainfall and the elements with uniform source distributions, showing the effect of local sources on relative variability.

10.2.2.2 Source Identification

A key question in assessing effects of increased coal burning on acid precipitation concerns the sources of the acidic components. It is
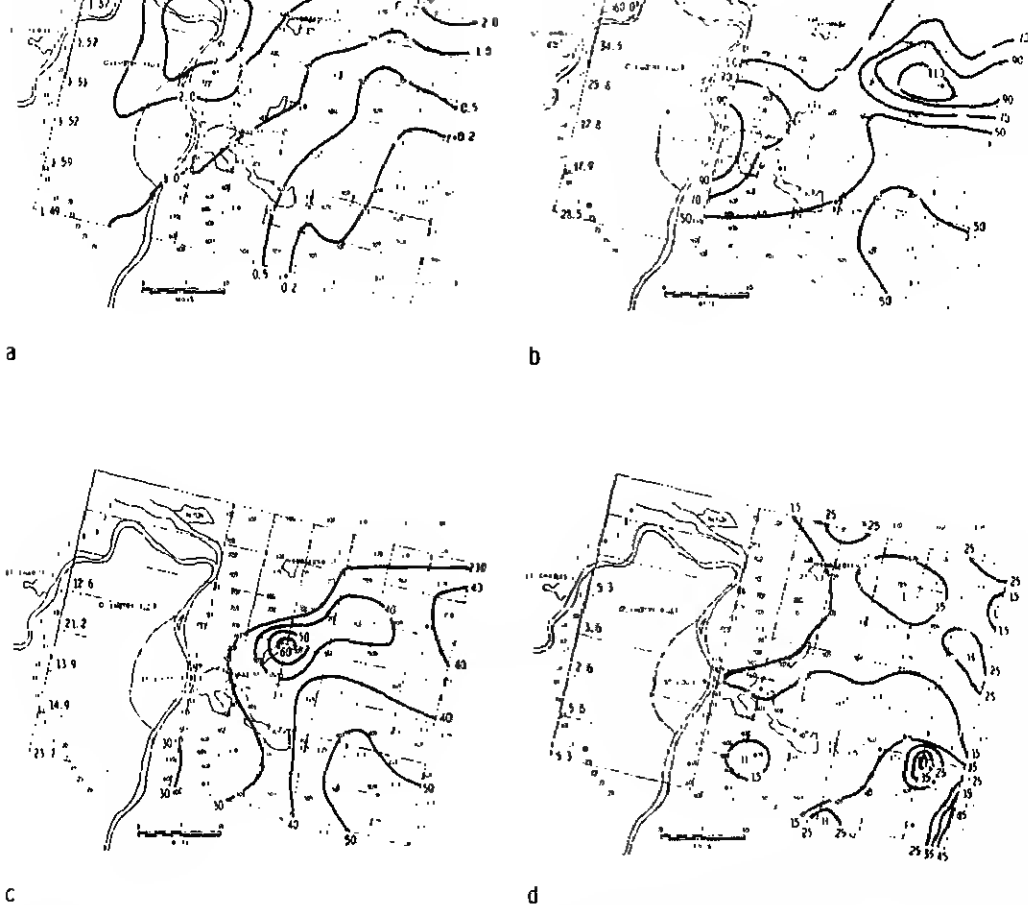
FIGURE 10.7 Measurements from late afternoon experiment of 23 July 1973. (a) rain amount, cm. (b) $SO_4^=$ concentrations, μmoles/l. (c) NO_3^- concentrations, μmoles/l. (d) NH_4^+ concentrations, μmoles/l.

important to know both the types of sources and their geographical locations, so proper decisions can be made regarding alternative energy sources and emission controls.

The identification of both area-wide and local sources of trace elements in St. Louis aerosols (Gatz, 1978) using factor analysis suggested that similar techniques might be applied to the constituents of precipitation. Initial results show that the chemical changes that occur when pollutant gases and particles enter precipitation alter the element associations that provide clues to source identity in aerosols. Thus,

sampling networks.

10.2.2.3 Recent Field Experiments in Rural Illinois

The ISWS carried out a Summer Chemistry Of Rain Experiment (SCORE-78) in rural central Illinois during June and July 1978. The objective of this work was to assess the variability of rainfall chemistry over single convective cells, and to understand how the precipitation composition is affected by meteorological parameters and air quality. Preliminary results emphasize that the acidity of precipitation is determined by both acidic and alkaline components. Thus, it will be necessary to predict the concentrations of both types of components and their relations to source strengths before one can predict precipitation acidity.

10.2.3 Discussion

The objective of most of the precipitation chemistry and scavenging measurements in MAP3S has been to provide the scientific understanding necessary to predict whether increased coal combustion will increase the acidity of precipitation.

The research summarized here indicates that:

1. Predicting the concentration or deposition of materials in precipitation, or removal efficiencies of airborne materials on an event basis still has a very high degree of uncertainty, but for seasonal or annual periods, deposition of airborne particles may be predicted with reasonable accuracy if particle size and airborne concentrations are known.

2. Analysis of only the soluble portions of rainfall constituents does not permit the identification of their sources by factor analysis.

3. During summer convective precipitation, urban SO_x and NO_x emissions appear to be deposited rather efficiently. A maximum deposition of urban particle emissions also occurs within 15 km of sources, but the efficiency has not been measured.

10.3 MODELING PRECIPITATION SCAVENGING

Precipitation scavenging is one of the more important pollutant sinks in the atmosphere. During a storm event, major fractions of pollutants drawn into the clouds are wet-deposited upon the surface. Indeed, as much as 30% of the total sulfur emitted over the U.S. during the summer

efforts related to the MAP3S study have dealt primarily with describing the wet removal of sulfate. One of the first models to be developed has relied heavily upon the observations from the Muskegon field studies (Chapter 10.1). Those experimental data suggest that the sulfate concentration in precipitation is related to the sulfate concentration of the air flowing into the clouds. The soluble, submicron, pollutant aerosol in this inflow air appears to be removed primarily by large collector particles, such as snowflakes or raindrops, sweeping downward through the cloud and capturing the small cloud droplets containing high concentrations of the aerosol.

The above concept of removal was considered by Scott (1978), who tried to parameterize sulfate removal for the three basic precipitation systems illustrated in Fig. 10.8. In the first case (Fig. 10.8a), ice crystals nucleate in the upper portions of the cloud, grow rapidly to precipitation sized particles, aggregate with each other, and accrete tiny cloud droplets. The accretion of small cloud droplets is assumed to be the primary growth mechanism for hydrometeors.[*] The sulfate incorporated into the precipitation is assumed to be predominantly that advected through the cloud base. Thus, sulfate pickup is assumed to come primarily through incorporation of the dirty cloud water in the lower portions of the cloud. This Bergeron or cold cloud is felt to be responsible for the majority of precipitation falling from layer type clouds over the continents (Mason, 1971).

For the second situation (Fig. 10.8b), the ice growth process is ineffective in initiating precipitation. Rain develops entirely through warm phase mechanisms (condensation and coalescence). A major fraction of the moisture and pollutants are assumed to be transported through the sides of the storm. For this second case, sulfate aerosol flowing into the storm at the higher levels are activated as condensation nuclei. This is in contrast to the first case, where ice crystals (collector particles) were assumed to activate on non-sulfur containing nuclei. The collector particles of Fig. 10.8b therefore have an initial sulfate concentration when they begin their descent through the lower portions of the cloud. Net sulfate pick-up is equal to the sum of the sulfate material activated in the collector particles at their formation altitude, plus the sulfate accumulated by accretion of the dirty cloud droplets near cloud base. Thus, this warm cloud is capable of removing more sulfate than the cold cloud.

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[*]Hydrometeors refer to ice or water particles large enough to fall from the cloud to the surface.
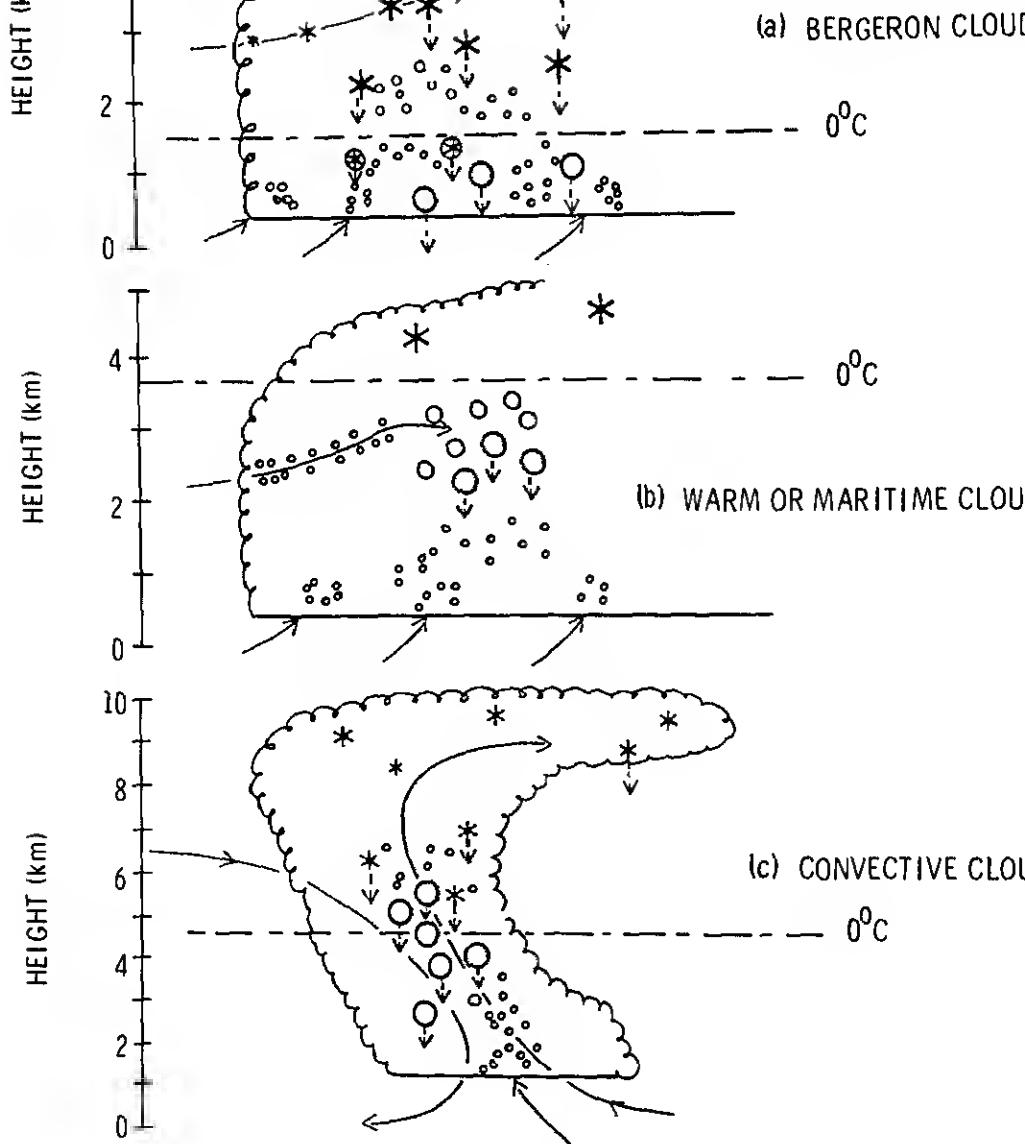
FIGURE 10.8 Qualitative description of synoptic situations envision
for the model. The symbols are as follows: (*),
particles; (*) in circles, melting ice particles; (O), liq
drops; (o), cloud droplets; solid lines with arro
trajectories of air flowing into the storm; dashed li
with arrows, motion of hydrometers relative to
storm. The vertical scale represents typical cloud depths

the individual warm or cold clouds primarily because those droplets that grow into collector particles have grown by coalescence in the lower portions of the cloud where the cloud water contains high concentrations of sulfate. Showery, summertime precipitation should exhibit removal characteristics of the convective cloud; that is, high concentrations of sulfate should be associated with convective showers affecting a small area (approximately 1-10% of the total surface area) at any one time.

These qualitative considerations have been expressed explicitly by Scott (1978) in terms of a washout ratio defined as the ratio of sulfate concentration in the precipitation water $(g_{sulfate}/g_{water})$ to the sulfate concentration in air below the cloud base $(g_{sulfate}/g_{air})$. Figure 10.9 illustrates the predicted variation of the washout ratio as a function of precipitation rate, J, for the cold cloud (curve 3), the warm cloud (curve 2), and the convective cloud (curve 1). For a fixed concentration of airborne sulfate and for a given precipitation rate, Fig. 10.9 predicts the lowest sulfate concentrations in precipitation originating as snow. Factor of 2 to 3 increases are predicted when precipitation develops by warm phase mechanisms in stratiform clouds. The greatest sulfate concentrations are predicted to occur in precipitation from convective clouds. The convective and warm cloud mechanisms would be most prevalent during the summer months while the ice growth mechanism would naturally occur during the winter.

Scott and Dana (1978) present the procedures for incorporating the washout ratio versus precipitation rate curves in Fig. 10.9 into parameterized formulas that describe wet removal rates for SO_2 gas and $SO_4^=$ aerosol. For the cold cloud, the sulfate removal rates are predicted to be proportional to $J^{0.7}$ where J is the precipitation rate. For the convective curve (curve 1), sulfate removal rates are predicted to be independent of precipitation rate. The majority of precipitation events (cold clouds) are expected to remove sulfate aerosol at the rate of near 40% h^{-1}, while SO_2 removal is predicted to be near 2% h^{-1}.

Data are becoming increasingly available for testing the concepts presented above. At ANL, studies of the distribution of pollutant concentration through individual rain events (storm "cross-sections") have led to a study of single-station precipitation chemistry, aimed at improving the conventional washout ratio and scavenging rate parameterization methods. Clearly, rain that first falls from a convective cell will be greatly enriched in sulfur (and in all other pollutants). As rainfall continues, pollutant concentrations will necessarily decrease, limited in the extreme by the reduction of the
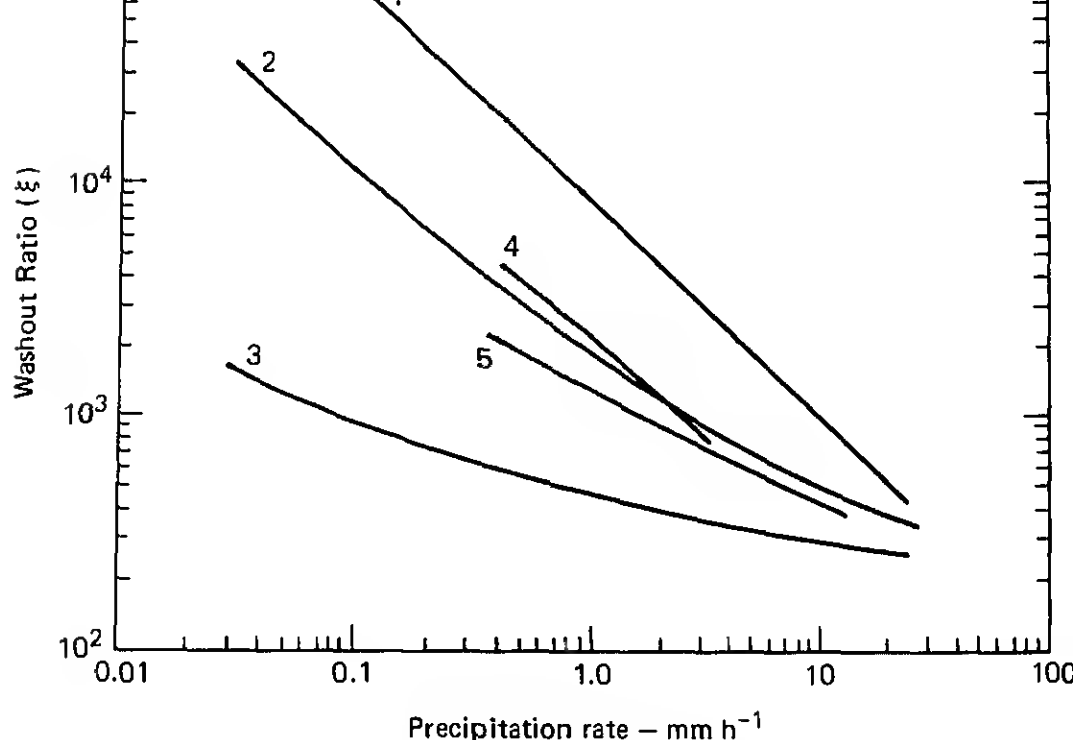
FIGURE 10.9   Washout ratio as a function of precipitation rate. Curve I
represents predictions for intense convective storms or
from clouds whose tops are warmer than 0°C; curve 2
represents predictions for storms where rain develops
without the assistance of an ice growth stage; curve 3 is
for storms where the ice growth process is necessary for
initiating precipitation; curve 4 is from observed ^{24}Na
concentrations in rainwater at Quillayute, Washington, on
April 5-6, 1970; and curve 5 is the same as curve 4 except
for data from December 11, 1969.

amount of pollutant left in the available air mass. At the end of any
particular rainfall event, concentrations might again rise, depending on
the type of the event, the maturity of the precipitation system, etc. On
the average, however, it is clear that the ratio of pollutant
concentrations in rain to concentrations in air at the same time, the
so-called washout ratio, must decrease with the amount of water
deposited in any single event (as illustrated in Fig. 10.9).

Hicks and Shannon (1979) have independently noted that the

to give reasonable results when compared with observations (Shannon, 1979). In addition, Hicks (1978) presents data for convective clouds which support the above contentions that the rate of sulfate removal is only weakly dependent on rainfall rate for convective clouds.

It is important to note that the above modeling considers in-cloud conversion of SO_2 to $SO_4^=$ to be of second order importance when compared to the removal of preexisting sulfate. In recent articles, however, MacCracken (1978) and Newman (1979) present intriguing arguments for the likelihood of substantial in-cloud SO_2 conversion to sulfate. The arguments are based upon examination of the sulfur budget over the MAP3S region and upon consideration of the available sulfate in the air that can be scavenged. In addition, Newman (1979) considers the acidity of aerosols and rainwater and concludes that it does not appear possible for rainwater to obtain its sulfur and nitrogen from aerosol sulfate or nitrate; both because the ambient concentrations of aerosols are too low and the acidity is insufficient to account for that found in rainwater. Based upon current estimates of transformation and dry deposition rates, Newman and MacCracken conclude: (1) that in-cloud conversion of SO_2 to $SO_4^=$ must be responsible for much of the observed wet sulfur deposition and precipitation acidity; and (2) an appreciable fraction of rainwater nitrogen and acidity may come from either nitrogen dioxide or nitric acid.

In response to the above claims of insufficient aerosol concentrations, Scott (1979) notes that by considering atmospheric convergence associated with storms, and the age of the air mass being scavenged, adequate concentrations of atmospheric sulfate should be present to account for precipitation water concentrations. Indeed, wet removal values of sulfur, nearly identical to those observed over the MAP3S region (i.e., 5% of emitted sulfur is deposited in precipitation during the winter, while in the summer about 30% is removed by rainfall), can be computed by considering increases in aerosol concentrations due to storm convergence. Precipitation acidity cannot, however, be explained with these storm-dynamic considerations.

Precipitation acidity and the rate of oxidation of dissolved species to the sulfate ion have a profound effect on the ability of rainwater to transport atmospheric sulfur to the ground. The modeling efforts of Hill and Adamowicz (1977) illustrate the strong influence of rainfall pH and ambient SO_2 concentrations on the removal rates of atmospheric sulfur dioxide. The half life of SO_2 during a storm event is shown to increase about ten-fold as the rainfall pH decreases from 7 to 4, and/or when the atmospheric concentration of SO_2 increases from about 1 to 100 ppb.

others, further notes that if an in-cloud bisulfite oxidation process occurs in the presence of ammonia the rain's capacity for sulfur is considerably increased.

Although it has been postulated based on some theoretical studies, the first documented, experimental evidence of possible in-cloud conversion of SO_2 to $SO_4^=$ has just been presented by Hales and Dana (1979) who have examined sulfate deposition patterns from summertime convective storms in St. Louis. The results are strongly suggestive that aqueous phase chemistry plays an important role in the scavenging process in warm clouds.

Thus, as more data become available, it is becoming clear that our understanding of sulfur wet removal and transformation mechanisms is still limited. The ability to predict wet removal of other combustion products such as nitrates is at an even more primitive stage of development.

The current generation of sulfur removal models are helping to identify the crucial properties that must be measured during storm events, and are providing important feedback for improving individual experimental design. The resulting improved experimental data are, in turn, expected to identify further weaknesses in model parameterizations that must be addressed.

In summary, the fate of SO_x and NO_x in summertime or wintertime storms is largely determined by atmospheric chemical conversion processes. Whether they be in-cloud or "clear air" conversions, these chemical conversions must be better understood before treatments of precipitation scavenging can progress much past the present, rather crude parameterization stage.

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From the beginning of MAP3S it was realized that energy-related pollutants have the potential to alter the weather and climate. Some of the modifications are quite direct, others are likely to be subtle. The range of possibilities is so large and unexplored, however, that the activities undertaken by MAP3S only serve to help better define the scope of the problem.

The most apparent effect is probably reduction of visibility. Evidence suggests that a very large fraction of the particles in the visibility-reducing size range are composed primarily of sulfate (Waggoner et al., 1976). It has been suggested that injection of pollutants higher into the boundary layer by use of tall stacks has led to deeper layers of polluted, low-visibility air. In turn, the atmospheric residence time of pollutants is then extended, because elevated layers can be isolated by low-level nocturnal inversions. This lengthened opportunity for pollutants to be transported and transformed may contribute to visibility obstruction over large areas.

Although visibility reduction can be an aesthetic and air safety problem, the impact of the aerosol on the atmospheric heating and cooling patterns may be more serious. Changnon et al. (1975) and Bolin and Charlson (1976) suggest that the reduction in solar radiation reaching the surface, because of increased levels of tropospheric aerosols, may reduce the length of the growing season by several days to several weeks. In addition to total solar radiation changing, the ratio of diffuse-to-direct radiation is changing (Wesely and Lipschutz, 1976), which may lead to biosystem responses. Whether the redistribution in solar energy absorption induced by aerosols leads to climatic effects remains uncertain. The EPA has recently initiated a major program (VISTTA) on this problem which will go far beyond the survey work described in Section 11.2 that MAP3S has undertaken.

A second major area of concern is potential modification to the precipitation mechanism. This matter was considered at the Chemist/Meteorologist Workshop in 1975 that served as the impetus for establishment of MAP3S (Slade et al., 1975). Because mechanisms are poorly understood, details are not clear, but the potential effects may be significant. Not only is precipitation chemistry affected, but cloud processes (including coagulation, nucleation, cloud condensation nucleii formation, and other aerosol surface phenomena) can be altered, leading to suspected changes in precipitation patterns and amounts. Also, possible changes in dew frequency and fog formation, which in turn may catalyze various plant diseases, may occur.

continued analysis of the scientific data derived from the multi-agency, multi-organization METROMEX program that had considered the scientific and socio-economic effects surrounding the St. Louis urban area. Based on results from these studies on a mesoscale area, we hope to be able to recommend areas for future research work on the potential for inadvertent weather and climate modification on the sub-continental scale.

11.1 INADVERTENT WEATHER MODIFICATION: METROMEX RESULTS

The St. Louis METROMEX program concerning inadvertent weather modification investigated certain research areas that are of concern to the MAP3S program goals. These areas ranged from the immediate impact of increased fossil fuel usage on local weather and climate to secondary and tertiary impacts of inadvertent weather modification on the socio-economic well-being of a region. The Illinois State Water Survey, with partial support from MAP3S, has published two volumes summarizing the 5-year research program.

The program summary addresses two issues related to inadvertent weather modification, namely, the scientific findings of causation and the socio-economic implications. These are the same issues to be addressed in the MAP3S program and, therefore, the METROMEX results can provide insight into some aspects of weather and climate modification associated with continued industrial growth and urban expansion. The reader is referred to these two reports (see Bibliography in Appendix C) for the various observations, measurements, and analyses that led to the descriptive summary presented in the following sub-sections.

11.1.1 Scientific Findings

The key research findings contain several suggested pathways between an urban-modified atmosphere and altered cloud and precipitation properties. Many of the data are presented as climatological sets which, by their cumulative nature, may mask more direct evidence of causative factors, but certainly provide guidance and set limits for the conditions associated with altered weather events. The physical interpretation of the observations led to the development of one or more hypotheses connecting urbanization and weather modification. Precise knowledge of the mechanism for natural production of precipitation is limited, and certainly the identification of those factors critical to inadvertent modification of the mechanism is also necessarily limited. The hypotheses developed are an attempt to explain the

when examining the potential effects of an urban-industrial complex on the atmosphere. The first of these is the development of small, non-precipitating convective clouds. The study of this type of cloud development can provide information on preferred areas for cloud initiation or enhancement. The second stage of cloud development is that of convective clouds that extend beyond the planetary boundary layer but do not produce organized precipitation. More frequently than not, these clouds are either observed as precursors to the development of precipitation or precede migratory precipitation systems as the atmosphere destabilizes. Finally, the urban area is suspected of influencing organized cloud systems that either are about to precipitate or are already producing rainfall across or in proximity to the metropolitan area. The direct influence of the metropolitan area on such clouds is difficult to ascertain because the increased rainfall arises from initiation of new showers or the enhancement of an existing, moving system. To quantitatively separate and study the contribution of these two possible mechanisms requires more sophisticated analyses than straight-forward rainfall observation.

The summer synoptic conditions that precede these three stages are those conducive to scattered cumulus activity. These conditions generally include the presence of a high pressure system centered southeast of Illinois thereby providing southerly, moist winds across the state. With time, the high pressure migrates eastward and is replaced by a more disturbed atmosphere, usually associated with a migratory frontal system approaching from the west. The capping inversion associated with the high is gradually dissipated and the lower troposphere becomes less stable throughout, with continous influx of moisture at low levels preparing the atmosphere for more active convection. Scattered convective showers are free to develop to great heights, but unless this condition is associated with a surface disturbance or a passing upper air trough, the showers will remain scattered and disorganized. With the approach of a synoptic scale disturbance the convective activity becomes more organized, resulting in either frontally associated or squall line precipitation.

There are three ways in which an urbanized area may affect clouds and precipitation: (1) direct modification of cloud properties by point and area source emissions of aerosols (CCN, IN),[*] water vapor, and heat; (2) direct modification of the planetary boundary layer thermodynamic structure by the urban heat island; and (3) mesoscale mechanical deformation of airflow resulting in converging flow in the lower layers.

There is evidence that all three exist, to some degree, in St. Louis.

concentration of cloud condensation nuclei, thus increasing the continental character of the clouds originating or passing over the urban area. Although there is evidence of low-level sources of ice nuclei, measurements in the troposphere indicate there may not be increased activity of this kind.

Water vapor is produced in many of man's urban-industrial activities, but this source is much smaller in summer than evapotranspiration from rural vegetation. Consequently, the urban surface represents a reduced source of moisture, and the vapor content of the surface boundary layer is generally lower than that in the country.

The very complicated group of processes involved in the heat balance at the urban surface does not necessarily predict uniformly warmer temperatures in the city during midday. However, there is evidence that in the lower boundary layer, a midday positive temperature differential does exist, particularly in cloudy weather. The urban-rural temperature difference has been found by aircraft measurements to exist throughout much of the depth of the planetary boundary layer.

Studies of the kinematics of the PBL wind fields during the afternoon revealed that St. Louis affects the winds in all types of weather conditions, producing areas of convergence and divergence, with their magnitude and location dependent on the ambient wind conditions. In general, the metropolitan area is found to be a zone of convergence, particularly in the late afternoon. These results suggest that updraft speeds at cloud base might be stronger and more sustained over the city by virtue of the convergence. Measurements of cloud updrafts support this, with higher updraft speeds and larger updrafts in urban clouds than in rural clouds.

These features of an evolving, perturbed boundary layer prepare the atmosphere for the appearance of the first clouds. The nocturnal inversion is observed to be stronger in rural areas than in the urban center where the heat island maximizes at night. In the early morning, the solar radiation in the city on a relatively clear day (as evidenced from satellite cloud studies) begins to dissipate the inversion at the surface. The inversion is weakest in the urban center, and the morning heating allows surface air to reach the lifting condensation level (LCL) earlier than in a rural area where a much stronger inversion must be overcome. The urban surface, by virtue of its roughness characteristics and its slightly warmer temperature, produces an increased flux of heat and water vapor through mechanical mixing or through enhanced thermal transport. The boundary layer convergence is present over the city throughout much of the PBL, and increases in depth as the PBL increases

conjunction with the city-related mesoscale convergence, allows mixing of near-surface properties throughout the lower levels of the boundary layer. This process results in the formation of the first clouds of the day over the urban areas with bases coinciding with the LCL. Continued mixing of the lowest atmospheric layers produces cloud bases at the convective condensation level by early and mid-afternoon with higher bases over the urban center due to the warmer and drier environment.

The development of air mass showers follows the same scenario, but in a general atmospheric environment conducive to deeper convection. These clouds are commonly quasi-stationary and consequently are more responsive to localized perturbations in their immediate environment. Because these clouds are either stationary or very slow moving, a source of condensation nuclei will be available for transport by the subcloud-base kinematic flow leading to ingestion by the clouds and modification of the microphysics. Equally accessible to the cloud is the sensible heat released from the urban area. In other words, isolated shower activity is more readily related to the disturbed boundary layer and the urban effects more easily identified than with migratory, organized precipitation systems. However, the five-year METROMEX project data do not indicate that the major inadvertent influence in the precipitation pattern occurs in air mass shower conditions.

The next question is, do these urban influences exist in organized convective systems? The organized synoptic scale precipitation systems, squall lines and fronts, represent another aspect of atmospheric instability. The atmospheric baroclinicity, or degree of atmospheric stratification, is altered significantly in proximity to fronts and upper-level troughs. The boundary between contrasting air masses provides a mechanism for cloud and precipitation development that produce precipitation in an organized fashion over an area irrespective of the presence of the St. Louis metropolitan region.

It is known that any deep convection tends to deform the airflow around it, and that new cells occur preferentially in one or two quadrants around the cloud. The quadrant in which the new cloud formation occurs is closely related to the direction of the wind shear in the cloud layer resulting in either upwind feeder cells or downwind feeder cells. The urban effect on these cells depends on the location and character of these feeder clouds in the migratory system.

The major precipitation anomaly has been found to the east and most particularly to the northeast of St. Louis. The winds above the PBL in the summer are most commonly from the WSW through the NW. Thus

either the greater likelihood of additional rain through pre-line cloud initiations or through intensifying the migratory line by mergers with urban-affected cells. These results may be used to identify key atmospheric variables that must be measured to test the hypothesized precipitation modification at other locations. The key results provide implications for regional planning strategies regarding placement of new industrial growth. The impact of cloud and precipitation development on urban-suburban hydrology and water quality is a serious consideration for future siting of fossil fuel burning industries.

11.1.2 Socio-Economic Implications

The identified impacts associated with urban-altered weather and climate are summarized in Fig. 11.1. The figure indicates three levels of impacts. The direct impacts of altered warm season storms were observed by the extensive METROMEX instrumented network of meteorological instruments. The monetary value of these various impacts was not thoroughly assessed as part of METROMEX, but an example might be useful.

Following the heavy line in Fig. 11.1, enhanced hail was observed east of St. Louis with secondary impacts on decreased crop yields as well as increased insurance payments to farmers. Of itself, this impact is not beneficial since the corn losses average 0.6 bu/acre and soybean losses 0.2 bu/acre. These losses resulted in insurance premiums in the area about 12% greater than unaffected areas.

However, one of the direct impacts of more total rain is increased crop yield. The net effect of these competing altered weather factors is an average increase in yields for corn and beans of 3% and 4%, respectively. Use of these figures coupled with average 1975 grain prices result in a net $2.2 million per year gain for the 2-county downwind area. The example illustrates the complexity of addressing the intricacies of weather impacts. This type of assessment is extremely valuable in the formulation of alternative strategies for urban-industrial development in a region. While it is not part of the MAP3S research effort, such evaluation efforts are a vital part of the continued research on identification of man's influence on his environment.

11.2 ATMOSPHERIC TURBIDITY

Episodes of increased atmospheric turbidity in the Midwest and the Northeast commonly cause reduced visibility, greater whiteness of the cloudless sky, and a decrease in the solar radiation reaching the surface
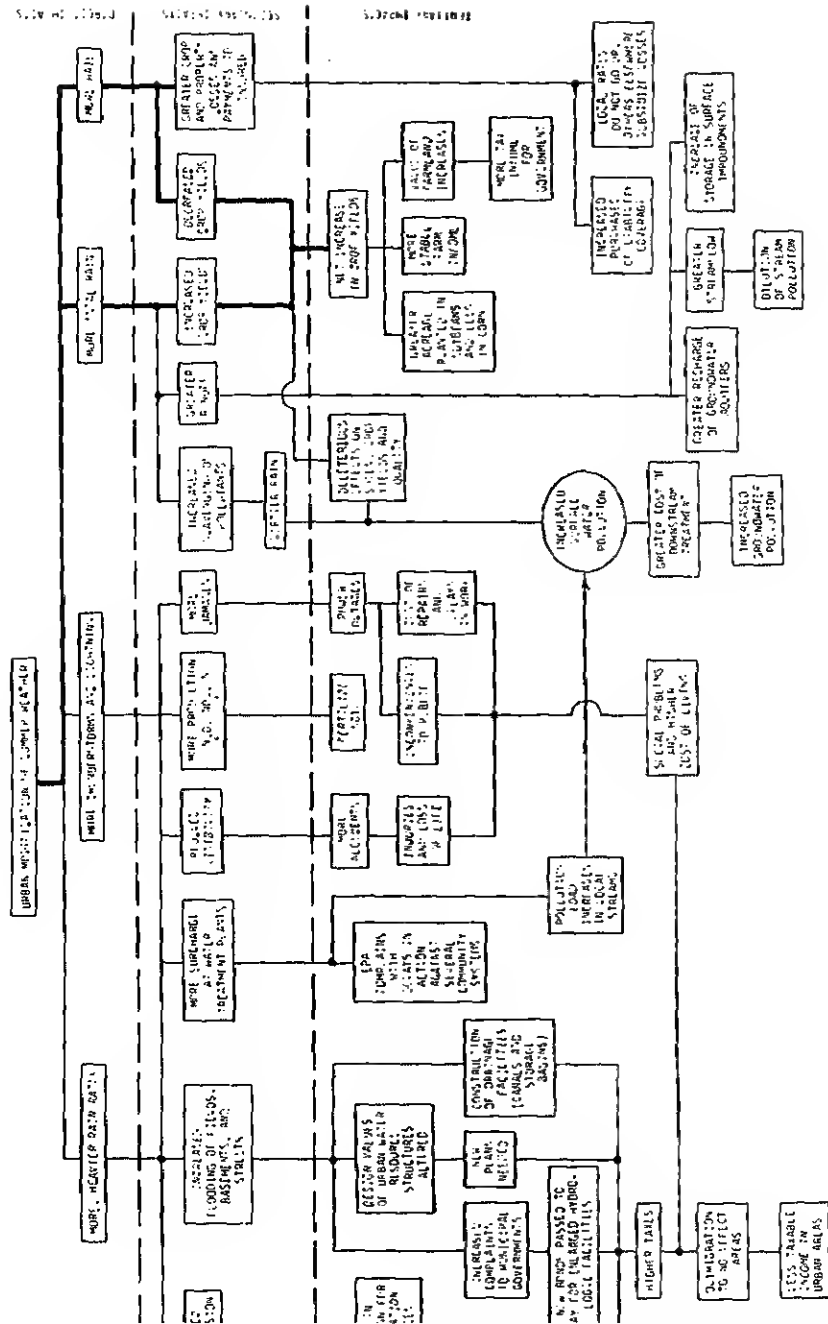
Various socio-economic impacts from inadvertent weather modification as identified during the METROMEX project.

of each "episode" appears to be a fairly constant proportion of the total airborne particulate matter (Charlson et al., 1974).

Methods of observing haze include use of Volz sunphotometers (Flowers et al., 1969) and estimates of surface visibility (e.g., Hall et al., 1973). However, data from Volz sunphotometers in the MAP3S region are no longer easy to obtain, and visibility observations usually are not highly accurate estimates of haze intensity, especially when a representative sample of the entire lower atmosphere is needed.

Therefore, as a means of evaluating the extent of the visibility problem, MAP3S established a network of turbidity sensors in the northeast. From the spring of 1977 until late fall of 1978 (encompassing the operation period of the SURE surface network), the network of sensors for measuring solar radiation has been operated in and near the MAP3S region to provide accurate quantitative estimates of the intensity of turbidity, its spatial and temporal variability, and its effects on solar radiation received at the surface of the earth. The data on atmospheric turbidity will be tabulated and provided to the MAP3S data bank (Chapter 13.1) so that these data can be correlated with information gathered from other observation programs.

11.2.1 Measurement Techniques and Implementation of the Network

The sensor used was a silicon photocell assembly that automatically provided both direct-beam (I) and diffuse (D) solar irradiance (ANL, 1976, 1978). Figures 11.2 and 11.3 illustrate the type of recording produced. The sensor is shaded every five minutes, causing a spike on the strip-chart record corresponding in length to the magnitude of I. This direct component can be reduced significantly by haze, although the diffuse component usually increases to compensate for 60-70% of the loss (Wesely and Lipschutz, 1976). Only cloudless and partly cloudy daytime conditions can be considered. However, since the diffuse component can be altered by nearby clouds on partly cloudy days, changes in I are of the most use. An aerosol extinction coefficient τ_a, derived from measured changes in I, is the primary parameter sought. Although the silicon photocell is not a commonly used device, changes in I and D as measured by the more common instruments can be computed easily from the measured values of τ_a. Thus, while the silicon photocell was chosen for use because of its low cost and east of operation, data from instruments operated by the National Weather Service can also be used to determine τ_a.

The network was limited to ten stations due to logistical constraints, so the locations were chosen to make optimum use of the available resources. A statistical objective sensor-placement technique was used
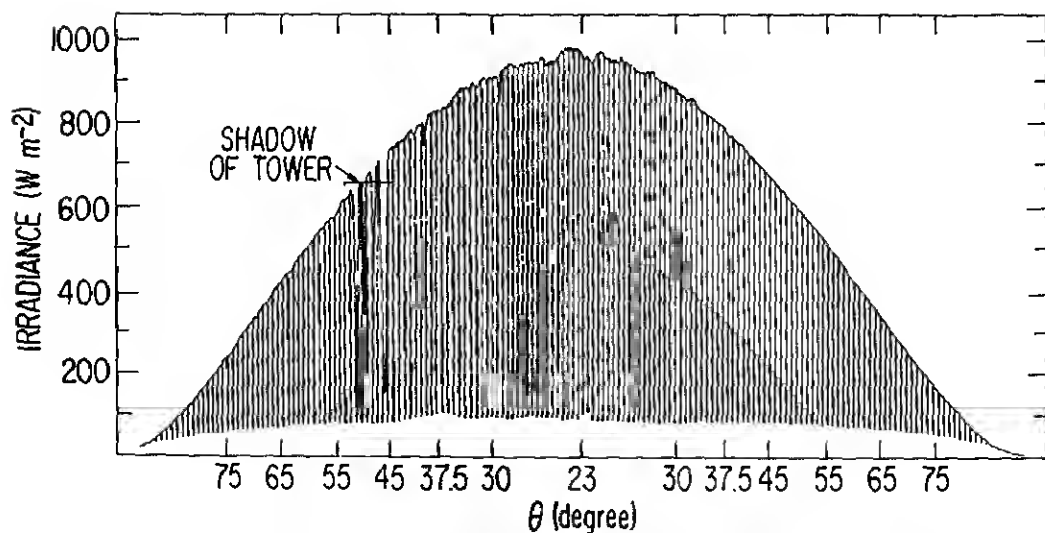
FIGURE 11.2 Strip-chart output of the silicon cell assembly for a day when very little haze was present. Although labeled in terms of solar zenith angle, the horizontal axis actually corresponds to a constant value of time per unit length.
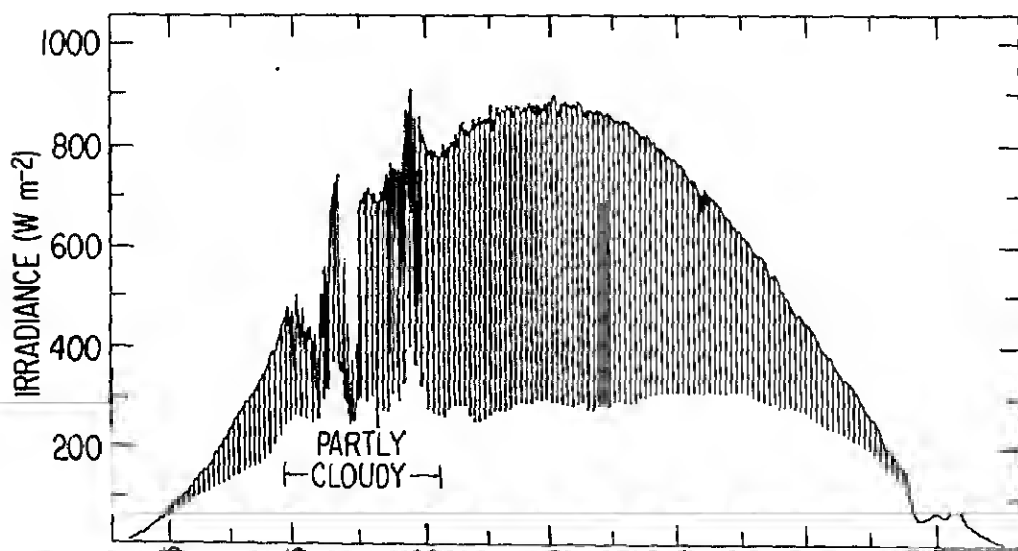
sunphotometers during 1972 and 1973 provided the raw information needed. Only data for the months May through September were used, times when the more severe turbidity or haze episodes associated with stagnant air masses are normally found. The final sensor locations, listed in Table 11.1, are shown in Fig. 11.4.

Operation of most network stations ceased in the fall of 1978 with the end of SURE's major observational program. In lieu of this MAP3S effort, the network of solar sensors recently established at NWS sites will be relied upon. Consideration is being given, however, to supplementing this network with 2-3 locations of silicon photocells, if

TABLE 11.1. Stations in the MAP3S Turbidity Network.

Site	Location
Argonne National Laboratory	41°42'N 87°59'W northeastern Illinois
Brookhaven National Laboratory	40°52'N 72°53'W Long Island
National Weather Service, Burlington, VT	44°28'N 73°09'W western Vermont
Miami University, Oxford, OH	39°33'N 84°46'W southwestern Ohio
NOAA/Atmospheric Turbulence and Diffusion Laboratory	36°02'N 84°14'W eastern Tennessee
Missouri Department of Natural Resources	38°40'N 90°44'W eastern Missouri
University of Guelph, Guelph, Ontario	43°39'N 80°25'W southern Ontario
University of Michigan Biological Station	45°33'N 84°41'N northern Michigan
Pennsylvania State University	40°48'N 77°75'W central Pennsylvania
University of Virginia	38°03'N 78°34'W
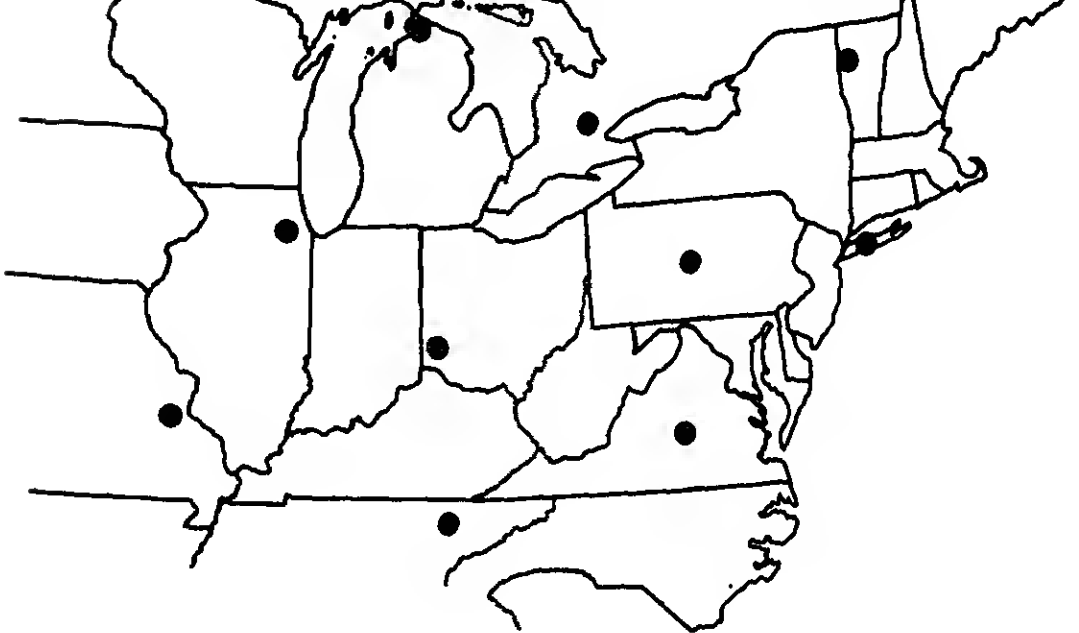
FIGURE 11.4 Location of MAP3S turbidity stations.

objective analysis of the 1977 and 1978 data indicates that such an augmentation would substantially improve regional coverage.

11.2.2 Discussion

Data analysis from the turbidity network has been slow due to the necessity of reading strip-chart records. Some preliminary results from 1977 are available, however.

The sensor-placement technique used to choose locations assumes that observations from different sensors are equally likely to be available on a given day; this has not turned out to be the case. When the skies were mostly cloudy or when equipment malfunctioned, useful turbidity data could not be obtained. At the Argonne station, data loss was due primarily to cloudiness, while losses at other sites, especially at St. Louis, Guelph, and Virginia, were due primarily to equipment problems. During one 214-day period of observation, the number of days with reliable turbidity data extractable from strip chart records ranged from 116 days for the Argonne sensor to 15 days for the sensor at the

sensor positions in the network, account needs to be made of the frequencies of observations at the different sites. To accomplish this, each sensor is in turn removed from the network simulation and the sub-network of the remaining nine is examined for explanation of the variance across the grid. The difference from the variance explained by the ten-station network is then multiplied by the frequency of observations of the omitted sensor, resulting in a relative value for each location as shown in Table 11.2. It is of interest to note how different the weighted evaluations are in comparison to strict ranking by incremental explanation of variance. St. Louis and Guelph are highly desirable as sensor sites, but the actual performance of the sensors there has caused the data to be quite limited.

Future plans include continuing evaluation of data from 1977 and 1978. These results will also be compared with data gathered in 1979 primarily by the NWS. Since acquisition of a sample size adequate for climatological purposes requires many years of operation, care must be used in interpretation of the results. A reasonable objective over the next few years will be to determine the general relationship between synoptic situations and the nature of the haze coverage, given the existing sources of contaminants that contribute to the production of haze.

TABLE 11.2. Sensor Evaluation

Location of Sensor	(a) Incremental Explanation of Variance	(b) Number of Observations	a x b
Brookhaven	.0116	64	.74
Argonne	.0055	116	.64
Miami	.0074	80	.59
Oak Ridge	.0062	76	.47
Pellston	.0050	72	.36
Burlington	.0056	64	.36
Pennsylvania State	.0044	69	.30
St. Louis	.0100	27	.27
Guelph	.0078	33	.26

Charlson, R. J., A. H. Vanderpol, D. S. Covert, A. P. Waggoner, and N. C. Ahlquist, "$H_2SO_4/(NH_4)_2SO_4$ Background Aerosol: Optical Detection in the St. Louis Region," Atmos. Environ., 8, 1257, 1974.

Flowers, E. C., R. A. McCormick, and K. R. Kurfis, "Atmospheric Turbidity Over the United States, 1962-1966," J. Appl. Meteoro., 8, 955, 1969.

Hall, F. P., Jr., C. E. Duchon, L. G. Lee, and R. R. Hagan, "Long Range Transport of Air Pollution: A Case Study, August 1970," Mon. Wea. Rev., 101, 404, 1973.

Shannon, J. D., M. L. Wesely and P. J. Brady, "Objective Sensor Placement for Sampling Regional Turbidity," Atmos. Environ., 12, 937, 1978.

Shannon, J. D. and M. L. Wesely, "Objective Re-evaluation of a Regional Turbidity Network," Trans. Joint APCA/ASQC Conference on Quality Assurance in Environmental Measurements, in press, 1979.

Wesely, M. L., "Measurements of Atmospheric Turbidity in an Arc Downwind of St. Louis," ANL-75-60, Part IV, Radiological and Environmental Research Division Annual Report, January-December 1975, 22p., 1976.

Wesely, M. L. and R. C. Lipschutz, "An Experimental Study of the Effects of Aerosols on Diffuse and Direct Solar Radiation Received During the Summer Near Chicago," Atmos. Environ., 10, 981, 1976.

Wesely, M. L., "On the Use of Silicon Photocells in the MAP3S Turbidity Network," ANL-77-60, Part IV, Radiological and Environmental Research Division Annual Report, January-December 1977, 118p, 1978.

thousands of sources, more than three hundred of which are power plants, emitting millions of tonnes annually of several different types of pollutants in a region one-third the size of the country, the complexity of the problem dictates the need for numerical (computer) models.

This chapter describes the efforts by MAP3S researchers to construct numerical models that quantitatively represent the fate of pollutants when influenced collectively by such processes as vertical and horizontal mixing and transport, transformation, and wet and dry removal processes. Earlier chapters have described the efforts being made to develop detailed parameterizations for each of the processes under highly focused conditions.* When trying to develop a comprehensive regional model, however, a series of compromises and simplifying assumptions is usually necessary to make the problem tractable for present mathematical methods and computer systems. This chapter also attempts to evaluate the uncertainties and limitations caused by these simplifications.

MAP3S has made a major commitment to the development of comprehensive numerical models. On the one hand we have attempted to improve the relatively simple <u>trajectory models</u> under development when MAP3S began. These trajectory models simplify the overall problem by treating the pollutants emitted by each source completely independently of the pollutants from other sources. Because this approximation makes the problem considerably more tractable on the computer, a great deal has been learned from such models about the factors influencing long range transport and regional pollutant levels. A particularly useful advantage of such models is the ability to relate the emissions to receptor points. However, this approach seriously limits the treatment of such possibly non-linear processes as chemical transformation and wet removal. Nonetheless, MAP3S is continuing to use and improve such models since they are relatively economical to run and may be able to answer some of the questions that must be addressed in assessment studies.

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*See Chapter 7.1 for discussion of representing vertical mixing depth, Chapter 7.3 for representing horizontal transport, Chapter 8.6 for representing pollutant transformation, Chapter 9.2 for representing dry removal processes, and Chapter 10.3 for representing wet removal processes.

development of grid models. In this approach, all sources and processes are treated simultaneously. While this allows a more realistic representation of atmospheric processes, it places heavy demands on computer resources and can thereby limit the range of studies that can be undertaken. Further, the grid size for this problem must necessarily be set at near 50 km to prevent unreasonable computer time requirements. This means that treatment of strong point sources will either be handled poorly at short distances from the source or that special measures must be taken to treat this situation.

In addition to the particular advantages and disadvantages of the two approaches being pursued by MAP3S, there are a number of problems that are common to both types of models. The most important difficulty is the mismatch between time and space scales of the processes being treated and the input and output data available to drive and test model behavior. Observations that may be used to compare with model performance include, for example, measurements taken at a local point (not a sub-regional area average) averaged over an hour or a day. On the other hand, source emission data are typically based on annual average release rates; meteorological data are taken twice per day at points about 200 km apart; and precipitation data often represent rainfall from a single cloud rather than storm average conditions. Further discussion on the requirements for testing various regional-scale models has been reported by Sheih et al. (1978).

Such complications make model testing extremely difficult. As a complementary approach to verification, MAP3S is therefore making efforts to upgrade treatment of model representations of individual processes based on results from focused field experiments in which conflicts between data and process representation can be reduced. This effort will provide increased confidence in model capability and permit evaluation of whether discrepancies with observations might be due to input data limitations. These efforts to represent the actual processes taking place and to understand the causes of discrepancies rather than to adjust parameters arbitrarily so that model results match available data, should permit considerably more confidence to be placed in model evaluations of the effects of control strategies than is justified with current models.

12.1 DEVELOPMENT OF TRAJECTORY MODELS

Regional-scale plume trajectory modeling forms the basis for two trajectory modeling approaches: statistical trajectory models, and regular (or simple) trajectory models. In statistical trajectory models,

a function of time since release, of a long time series of simulated individual tracer particle trajectories. In contrast, in regular trajectory models, dispersion, transformation and removal parameterizations are applied to the simulated individual trajectories as a function of time.

12.1.1 Statistical Trajectory Models

The original impetus in the development and use of statistical trajectory models was provided by the work of European researchers (Bolin and Persson, 1976). The method is very appealing because of the computational simplicity and efficiency, and because the meteorological data and the data resolution required by the model are wind and precipitation on the scales commonly observed. The statistical nature of the model, however somewhat limits the use of the results to determining the probable location of sources causing air pollution and acid rain over monthly to yearly periods rather than on an episodic basis.

Sheih (1977a) adapted the statistical trajectory technique to prediction of long-term regional patterns of sulfur pollutants in the eastern U.S. The primary differences from previous work were the use of puff-on-cell numerical dispersion techniques (Sheih, 1977b) for vertical integration and in the computation of wet deposition as a function of individual rainfall occurrences, rather than as a function of seasonal precipitation climatology.

Treatment of dispersion, transformation, and removal processes in the ANL statistical trajectory modeling efforts have been further improved in the Advanced Statistical Trajectory Regional Air Pollution (ASTRAP) model (Shannon, 1979). The primary refinements are inclusion of typical diurnal and seasonal variations in the vertical structure of the planetary boundary layer (a seasonally varying pattern of nocturnal inversion formation, deepening, lifting, and dissipation), typical diurnal and seasonal variations of deposition velocities of SO_2 and sulfate, based upon ANL field studies that also show deposition velocities roughly equal for the two pollutants (Figs. 12.1 and 12.2), diurnal and seasonal variations in the rate of transformation from SO_2 to sulfate (Fig. 12.3), and estimation of wet removal of total sulfur as a function of the half power of hourly precipitation. In addition, mass budget calculations of total wet and dry deposition and net mass flux across political or natural borders are calculated.

ASTRAP has been made more general by calculating trajectory statistics for a grid of virtual sources across the eastern U.S. Since long-term horizontal dispersion on a regional scale changes slowly across the grid, dispersion from actual source locations can be estimated by interpolation of gridded results. This means that numerous combinations
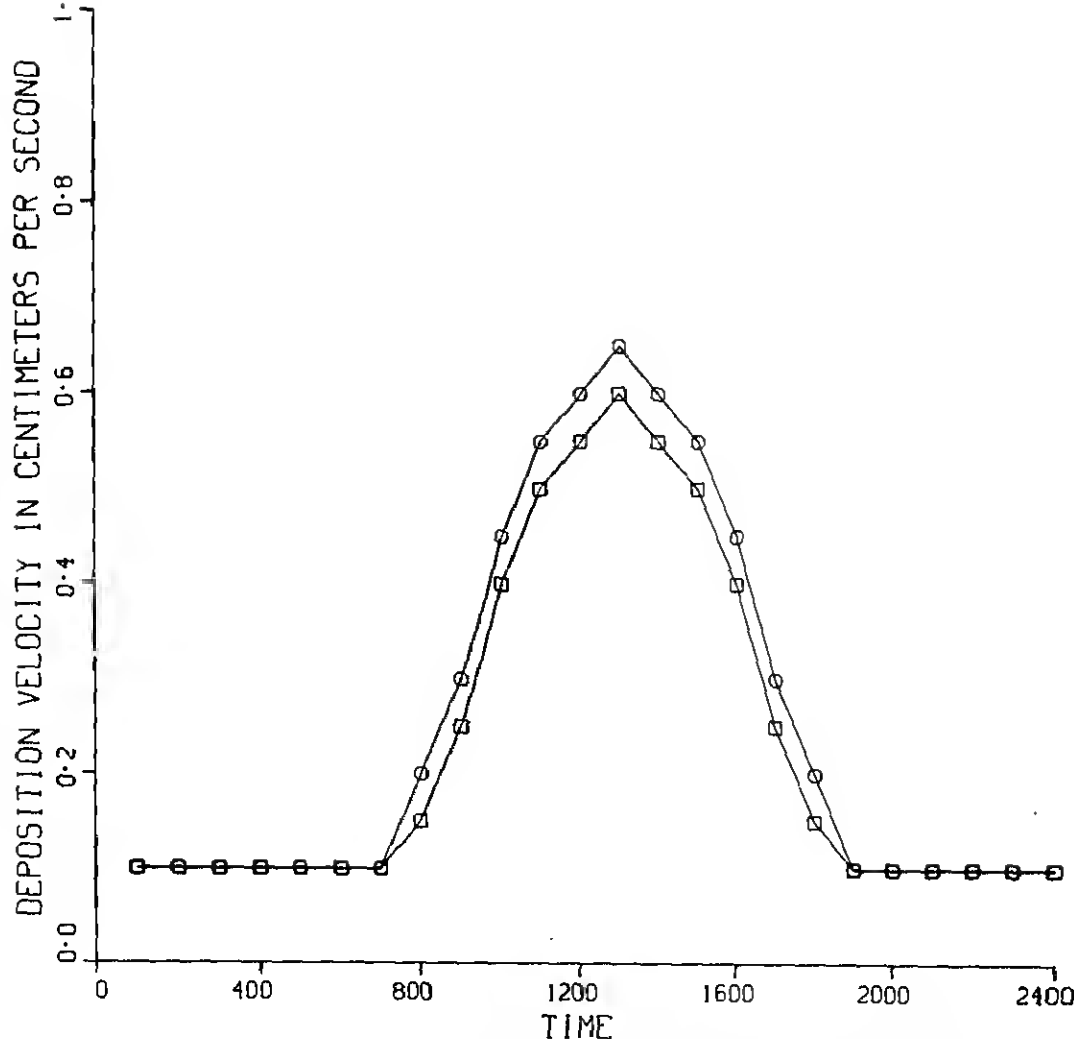
FIGURE 12.1   Diurnal pattern of deposition velocities for SO_2 (□) and $SO_{\bar{4}}$ (O) during winter simulations using ASTRAP model.

Sensitivity studies of ASTRAP indicate that the most important diurnal variation is that of atmospheric stability, because the nocturnal inversion essentially decouples pollutants aloft from surface removal processes. For tall sources, such as utility stacks, inclusion of the decoupling effect can reduce maximum predicted average concentrations of SO_2 or sulfate by as much as 50%. Inclusion of the diurnal variation of deposition velocities causes predicted concentrations to rise as much
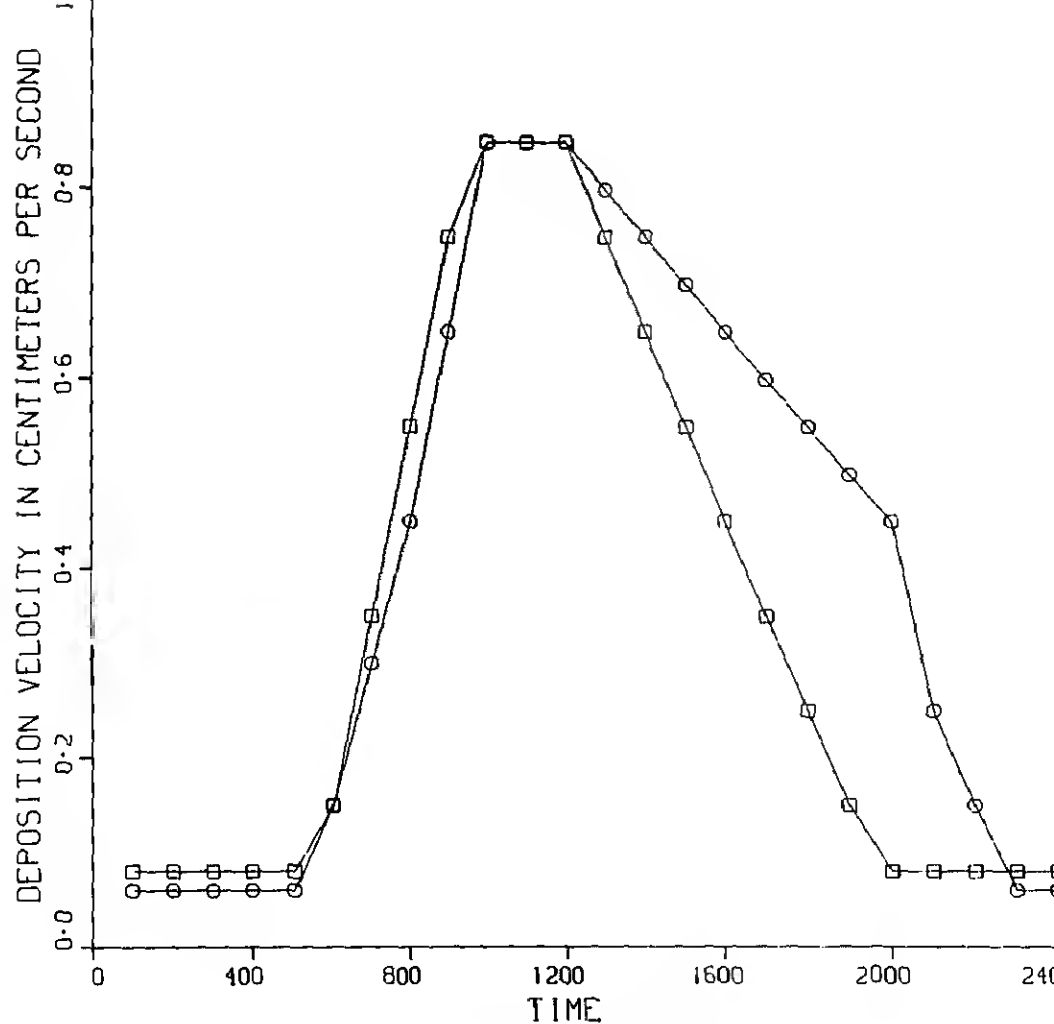
FIGURE 12.2 Same as Fig. 12.1, except for summer.

concentrations, a lower transformation rate increases SO_2 and decreases sulfate, and faster transport winds dilute both long-term concentrations. If no seasonal variation of emissions is modeled, the net effect is that winter SO_2 concentrations are reduced as much as 30%, while sulfate concentrations are reduced as much as 60%.

The sulfur budget studies summarized in Table 12.1 and shown in part in Figs. 12.4 to 12.7 indicate that the impact of U.S. sources on Canadian air quality is considerably greater than the impact of Canadian sources
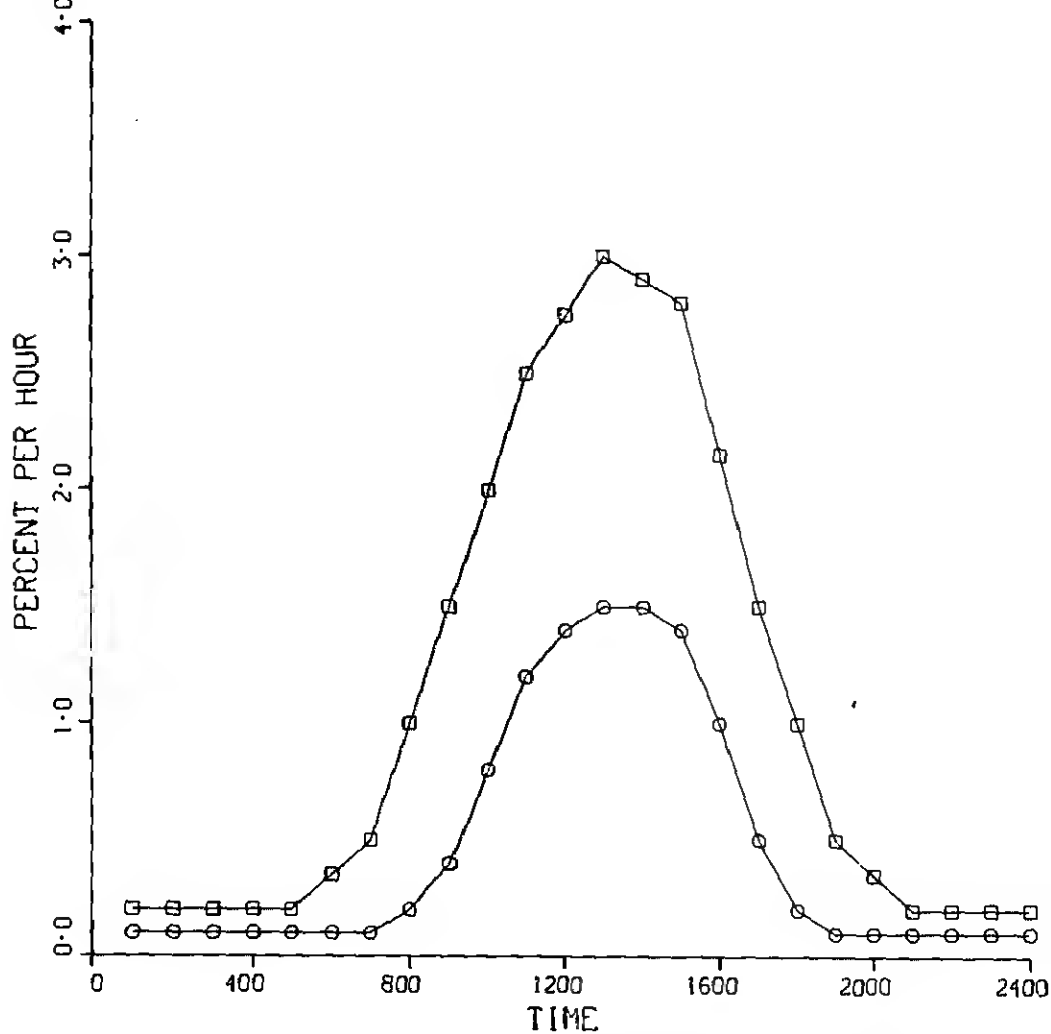
FIGURE 12.3 Diurnal pattern of SO_2 to $SO_4^=$ transformation rate for winter (O) and summer (□) simulations using ASTRAP model.

have not been adjusted to "tune" the model; the values used represen[t] estimates of actual physical processes, as determined by fiel[d] investigations and climatological data. The emission data used contai[n] considerable errors in location and effective emission heights must b[e] estimated; a better emission data base might change results considerabl[y] without any adjustment of parameters. Since the emission inventory tha[t]

		U.S. Wet dep (kT)	U.S. Dry dep (kT)	Net Flux (kT) U.S.-C Border	Net Flux (kT) Coasts
Eastern U.S. emissions (2970 kT S/quarter)	Summer	600	390	550	1420
	Winter	500	180	410	1880
Southeastern Canada Emissions (365 kT S/quarter)	Summer	46	15	~86	
	Winter	52	11	~81	

12.1.2 Trajectory Models

MAP3S regular trajectory models include a PNL puff model for long-term assessments, a PNL linear plume segment model for both long and short term assessments, a PNL nonlinear plume segment model, which treats the physical processes of wet removal more rigorously for short term assessments, and the ARL transport and dispersion model, as modified and expanded by BNL.

The PNL puff model sums the effects of puffs to the grid cells below (Powell et al., 1979). Horizontal turbulent diffusion is not modeled, as synoptic-scale wind variation is assumed to be the dominant mechanism for horizontal dispersion. Vertical diffusion is Gaussian between upper and lower bounds with a specified diurnal cycle of stability and mixing depth; eventually the puff is assumed to be well mixed. Dry deposition is computed by a source depletion algorithm, modified by Horst (1979) to approximate the removal at the surface. The deposition velocities are calculated from surface roughnesses and stomatal resistances, requiring gridded maps of each. The surface roughnesses have been estimated by ANL and the stomatal resistances depend on vegetative characteristics and stability (Sheih et al., 1979). Wet deposition of SO_2 is a linear function of SO_2 mass and precipitation rate; wet deposition of sulfate is linear in sulfate masses and proportional to the 5/8 power of precipitation rate. The SO_2-$SO_4^=$ transformation rate is a function of source type, time of day, and time since release. In addition to SO_2 and $SO_4^=$ long-term concentrations and deposition, the PNL puff model computes rainfall pH.
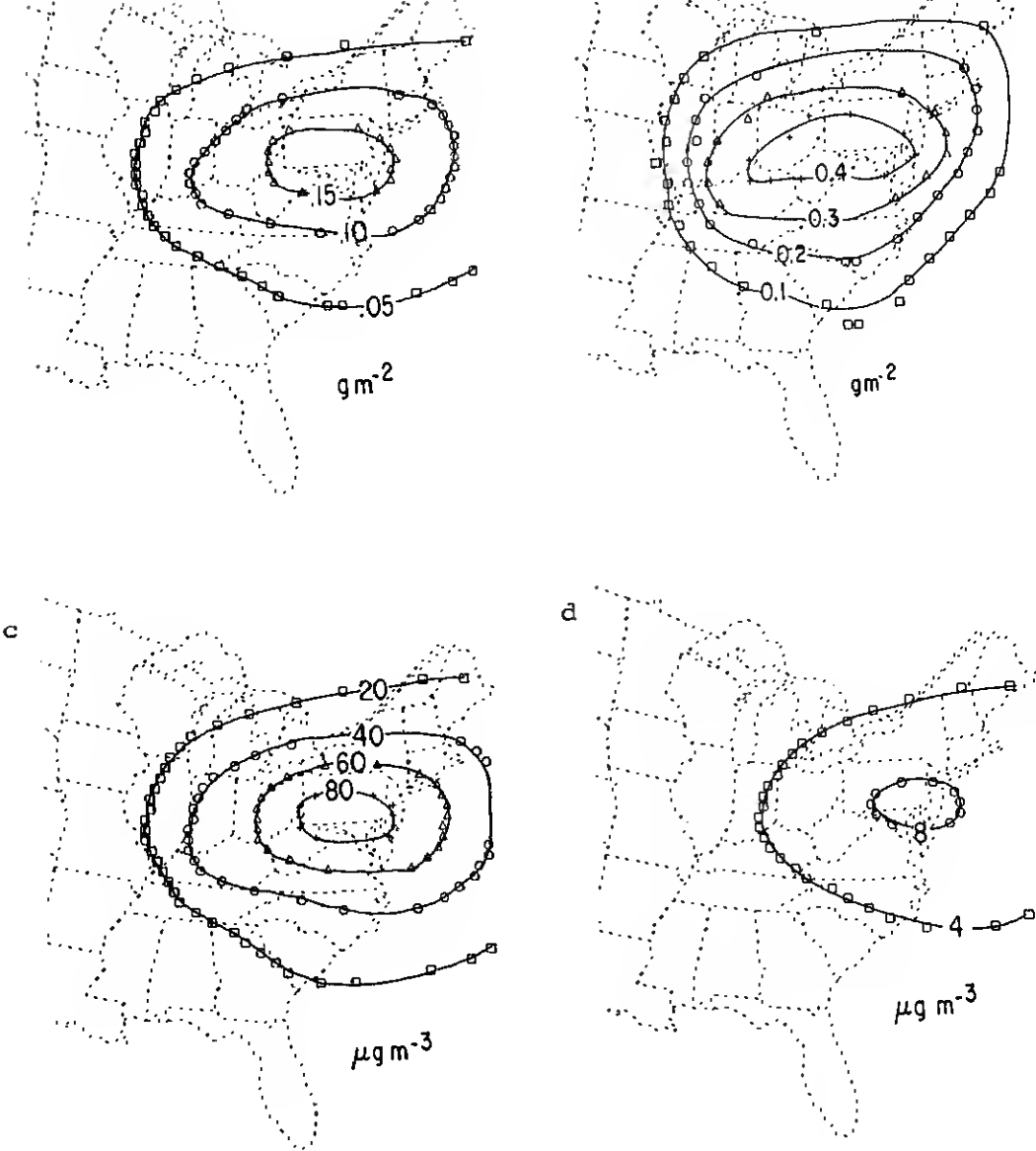
FIGURE 12.4 Sulfur budget components due to U. S. emissions for three month winter simulation using ASTRAP model: (a) dry deposition, (b) wet deposition, (c) average SO_2 concentration, (d) average $SO_{\bar{4}}$ concentration.
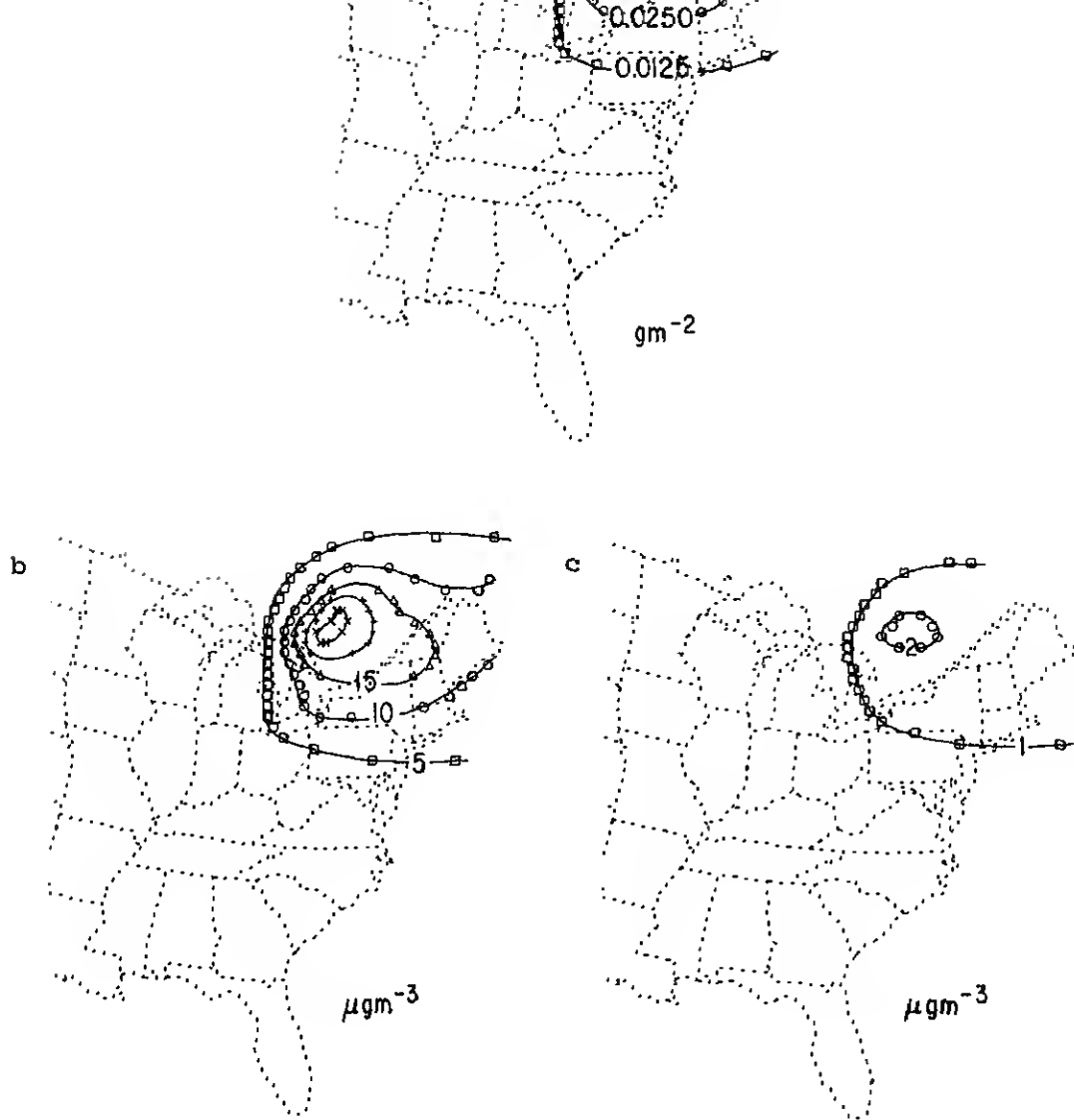
FIGURE 12.5 Sulfur budget components due to Canadian emissions for three month winter simulation using ASTRAP model: (a) dry deposition, (b) average SO_2 concentration, (c) average SO_4^- concentration.

a ... gm⁻² ... 0.3 0.2 0.15 0.1 0.05

b ... gm⁻² ... 0.5 0.4 0.3 0.2 0.1

c ... μg m⁻³ ... 20 40 60 100 80

d ... μg m⁻³ ... 4 8 12 16 20
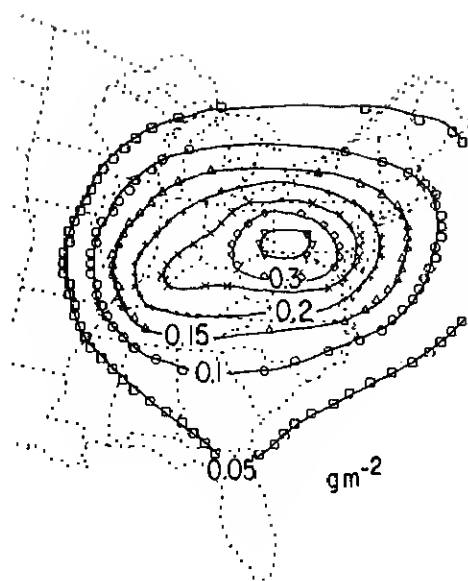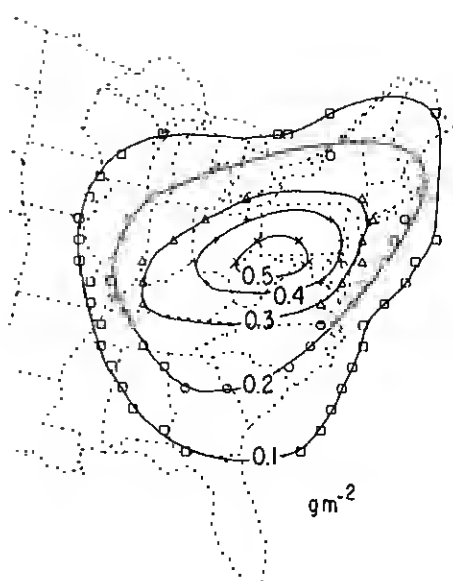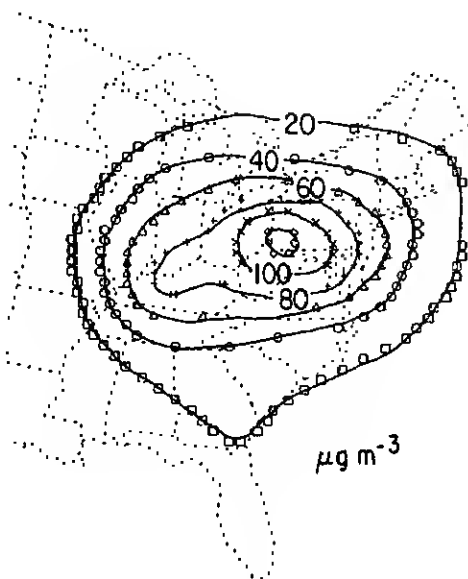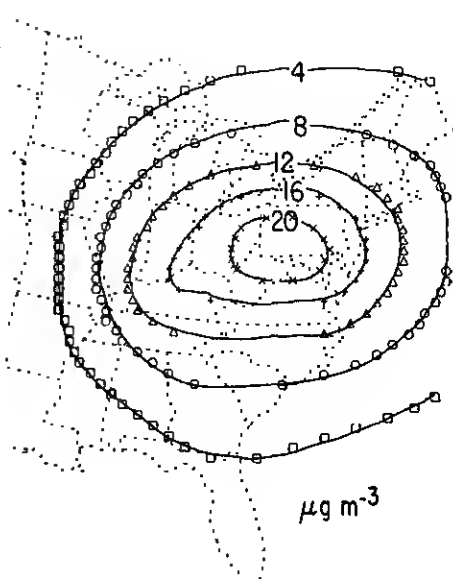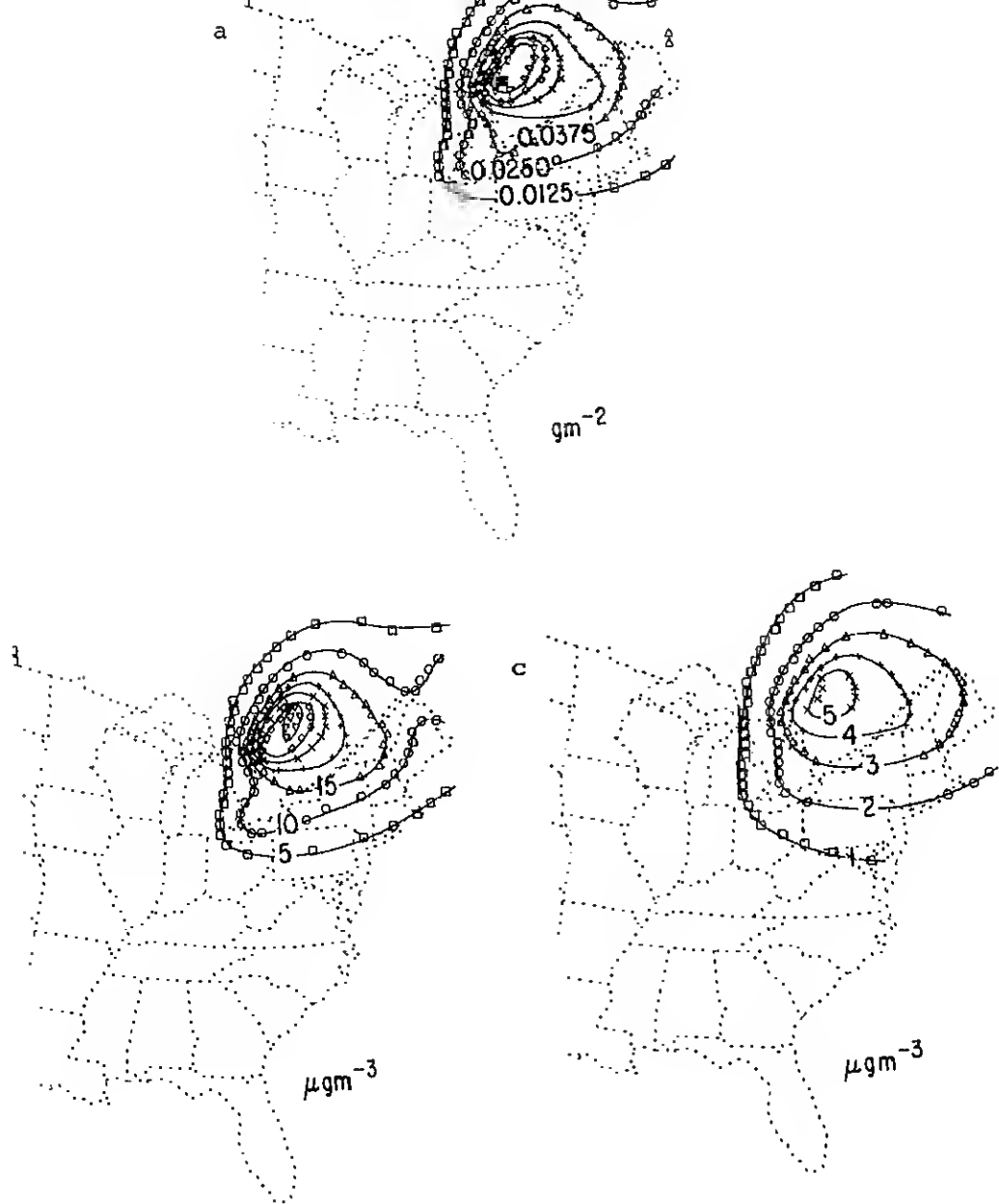
FIGURE 12.7   Same as Fig. 12.5, except for summer.

concentrations during the first two SURE intensive measurement periods (August and October, 1977). Figures 12.8 and 12.10 show the observed $SO_4^=$ concentrations, based on measurements taken by the SURE 54 station network.[*] (Data from about one-quarter of the stations during each month were judged insufficient to construct a meaningful monthly average.) Figures 12.9 and 12.11 show the results of model simulations for the same months using available meteorological and precipitation data, but not yet updated source emissions information. Concentrations at the center of the region tend to be simulated quite well, whereas simulated concentrations on the southern and western boundaries are too low, probably due to deficiencies in the emissions information and present limitations on domain size.

The main difference between the PNL puff model and the PNL linear plume segment model is that the latter parameterizes horizontal diffusion as a Gaussian function of stability and can be used for either long- or short-term assessment.

The more detailed precipitation chemistry in the nonlinear plume segment model requires local SO_2 concentrations in order to vary wet removal with water solubility of SO_2. Plumes must thus be superimposed during calculations, rather than after calculations. In addition the model requires knowledge of rainfall pH and temperature. The detailed calculations limit the model to short-term assessments investigating episodes of possible acid precipitation.

The BNL Long and Short Range Air Quality Model (Meyers et al., 1978), an extension of the ARL trajectory model, calculates SO_2 and $SO_4^=$ concentrations from the cumulative effect of repeated simulated trajectories. Horizontal trajectories are calculated from observed winds in the mixing layer; horizontal diffusion is specified as Gaussian. Vertical diffusion is calculated using eddy diffusivity in a modified Crank-Nickelson finite-difference technique; dry deposition velocities are chosen larger than those in other similar models in order to approximate both wet and dry deposition. Linear transformation of SO_2 to $SO_4^=$ is included.

The model has been run with emission and population projections to estimate population-weighted cumulative exposure (see Section 12.2); the air quality results can be used with a health effects model to estimate the human mortality and morbidity associated with different energy scenarios.

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[*]MAP3S would like to gratefully acknowledge the cooperation of EPRI

12.8 Contours of surface $SO_4^=$ concentrations for August 1977 based on observations from the
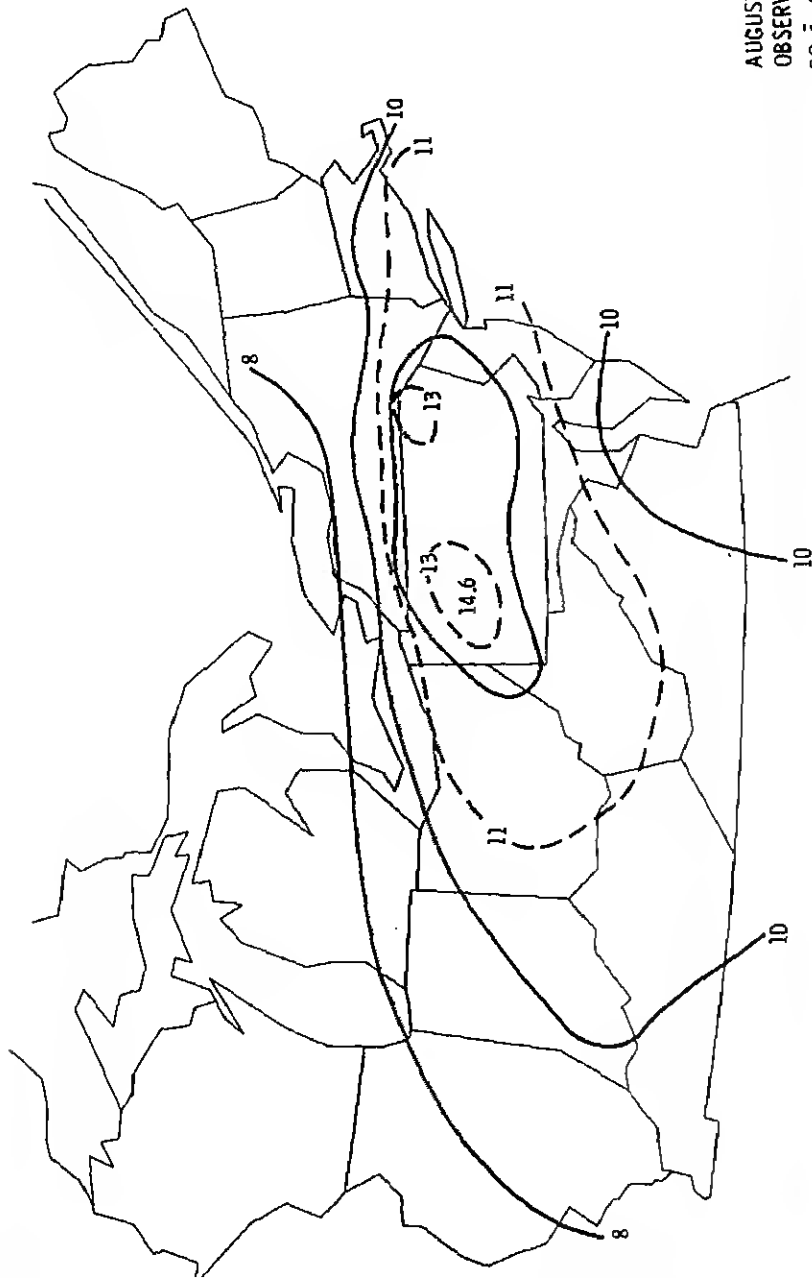
AUGUST, 1977
OBSERVED
$SO_4^=$ ($\mu g/m^3$)

AUGUST, 1977
PREDICTED
$SO_4^=$ (μg/m³)
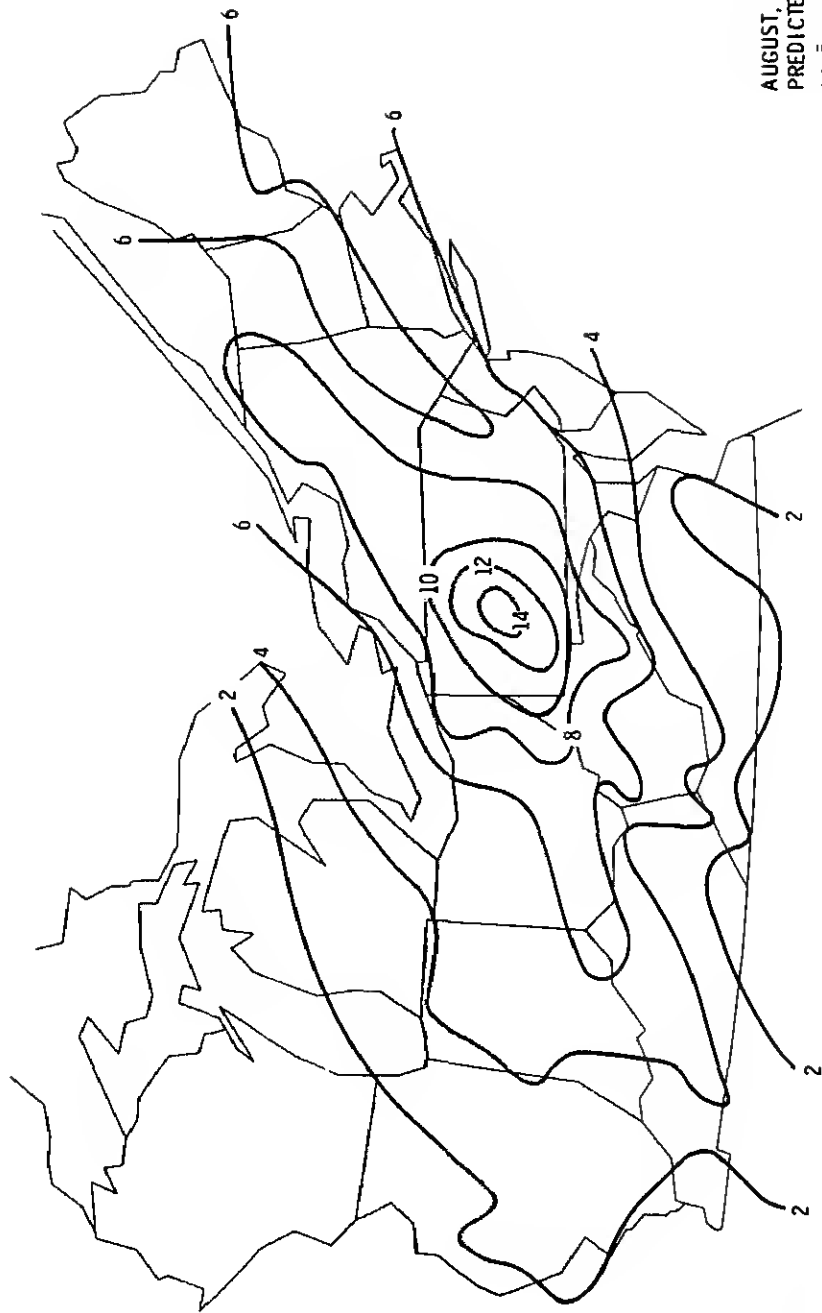
FIGURE 12.9 Contours of surface $SO_4^=$ concentrations for August 1977 based on PNL model simulations

OCTOBER, 1977
OBSERVED
$SO_4^=$ ($\mu g/m^3$)

FIGURE 12.10 Same as Fig. 12.8, except for October 1977.

OCTOBER, 1977
PREDICTED
$SO_4 =$ μg/m³
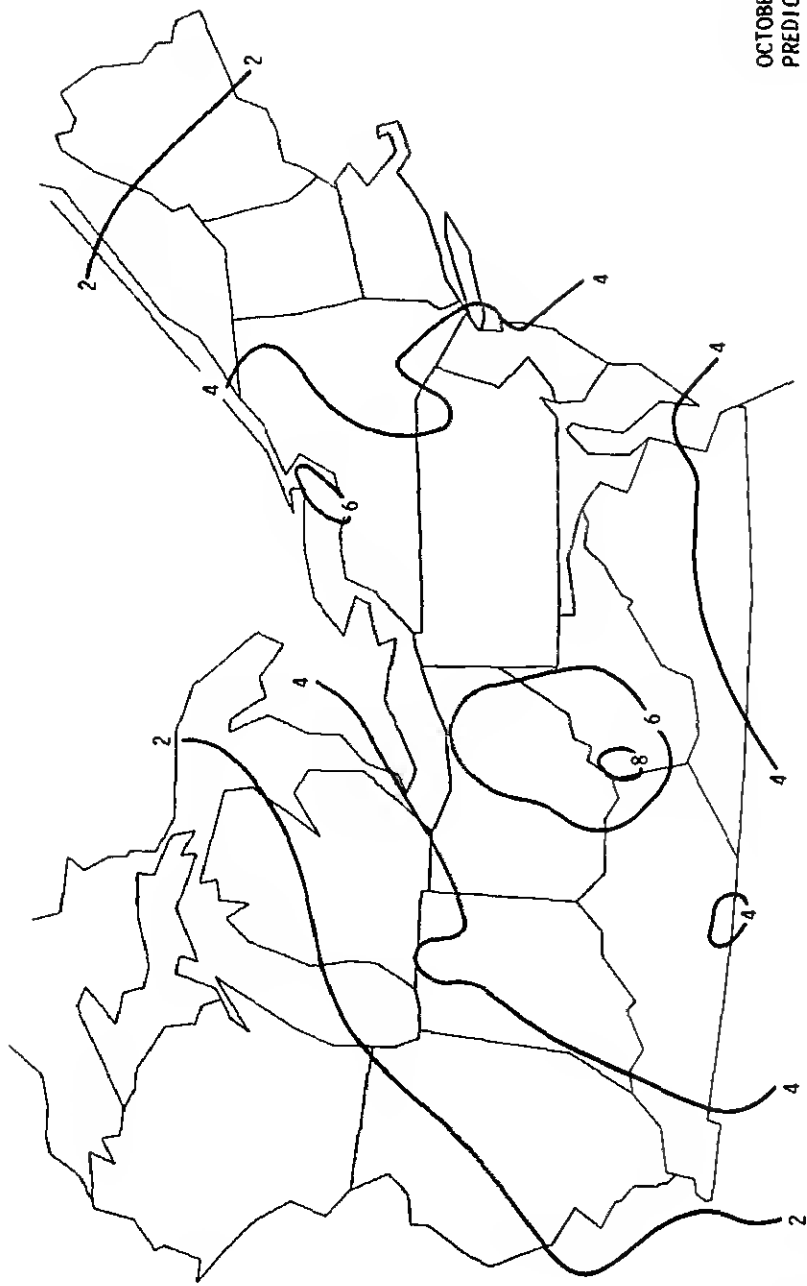
FIGURE 12.11 Same as Fig. 12.9, except for October 1977.

Simulations with the BNL air quality model show SO_2 patterns (Fig. 12.12) to be "spiked" or local, while the sulfate patterns (Fig. 12.13) are smoother and more regional. These simulations show results for emission inventories projected to 1990 as part of the DOE National Coal Utilization Assessment (NCUA). The predictions have been subjected to a priori and a posteriori analyses of calculation uncertainty. Reference cases were calculated and simulation uncertainty was documented based upon critical parameter values (prior analysis). The reference cases were compared with data and conditioned (posterior analysis) values of the critical parameters were chosen to minimize population-weighted differences between calculations and observations of pollutant concentration.

CALCULATED SO 2

SCENARIO   1990 NCUA UTILITY AND INDUSTRIAL
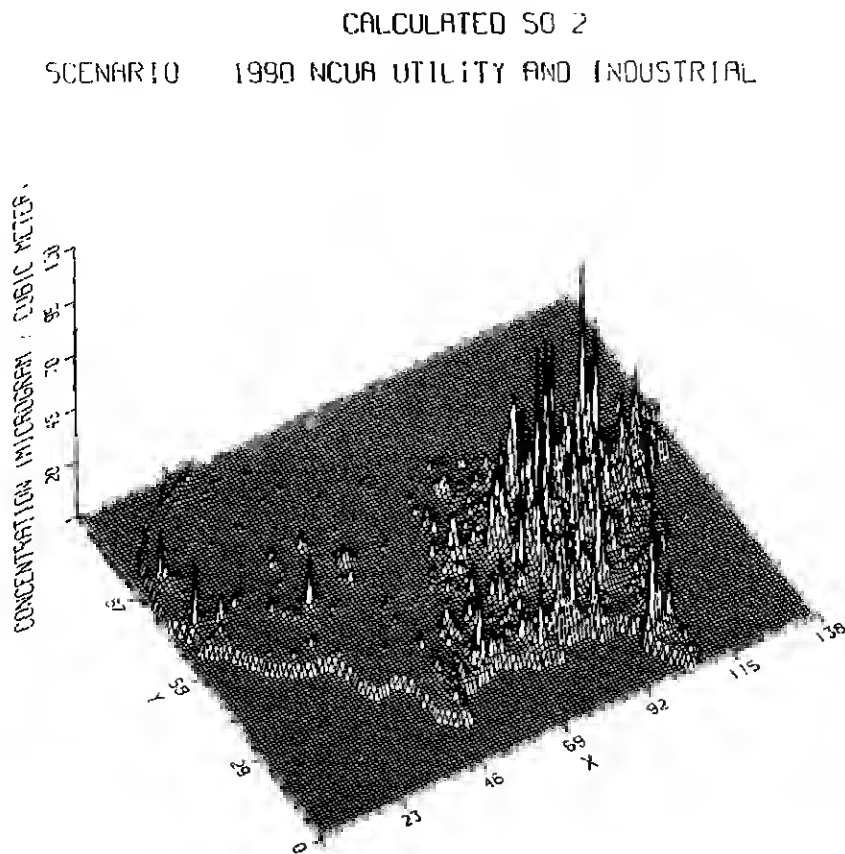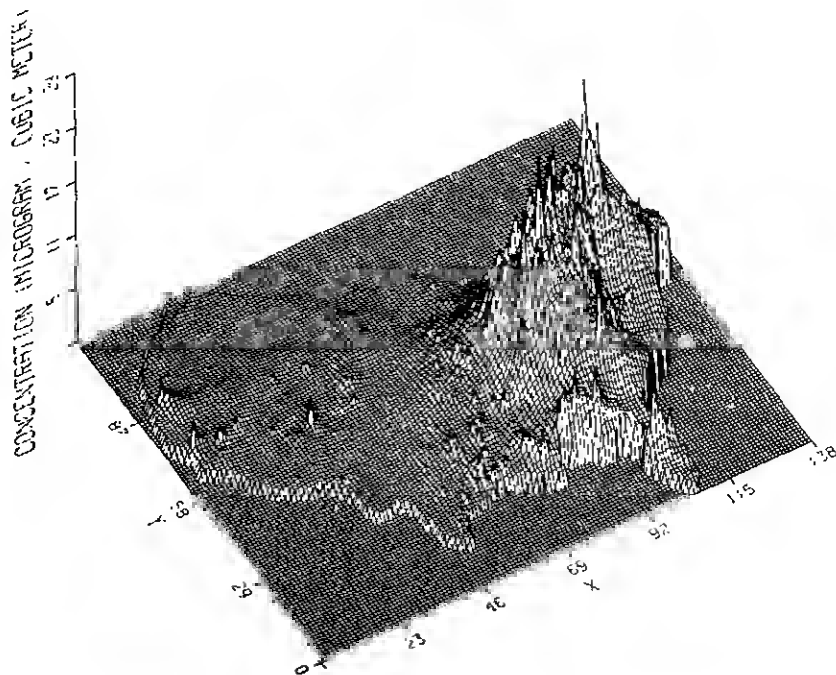
FIGURE 12.13 Same as Fig. 12.12, except for $SO_4^=$.

12.2 APPLICATION OF TRAJECTORY MODELS

Section 12.1 dealt with development and verification of trajectory models. To better understand the function that numerical models might play in assessment activities, a number of model applications have been undertaken. These each have focused on addressing particular questions.

12.2.1 Residence Time of Sulfur in the Northeastern U. S.

In a simple box under steady state conditions, the traditional concept of residence time can be applied to evaluate the mean turn-over time of sulfur dioxide. However, the concept is not particularly useful in the real world since meteorological conditions (and related transformation and sink processes) are not in steady state. Schwartz (1979) has extended

States have been used as an example of the application of this definition. The input to this treatment is a grid of concentrations of SO_2 and of sulfate attributable to each of 283 large SO_2 sources in this region. (Figure 4.1 shows a slightly smaller, but comparably dispersed, array of emission sources.) The model parameters utilized in calculating these concentrations are as follows:

Mixing height:	1000 m
Primary sulfate emissions:	2% by mole
SO_2-$SO_4^=$ conversion rate:	0.5% hr^{-1}
SO_2 deposition velocity:	3 cm/sec[*]
$SO_4^=$ deposition velocity:	0.3 cm/sec[*]

The trajectory-diffusion model of Heffter et al. (1975) was employed, using as input data meteorological measurements for July 1974.

Figure 12.14 shows the field of SO_2 concentrations resulting from exercise of the model. The residence time of SO_2 within the region, as a function of location of the source, can be computed as

$$\tau_k = Q_k^{-1} \, h \sum_{ij} c_{ij,k} \, a_{ij}$$

where τ_k is the residence time of SO_2 emitted from the kth source,

Q_k is the strength of source k,

h is the mixing height,

$c_{ij,k}$ is the concentration in the ij^{th} grid box attributable to the kth source, and

a_{ij} is the area of the ij^{th} grid box.

The residence times computed are only slightly a function of source location, being dominated largely by SO_2 dry deposition (1000 m/3 cm s^{-1} = 9 hr).
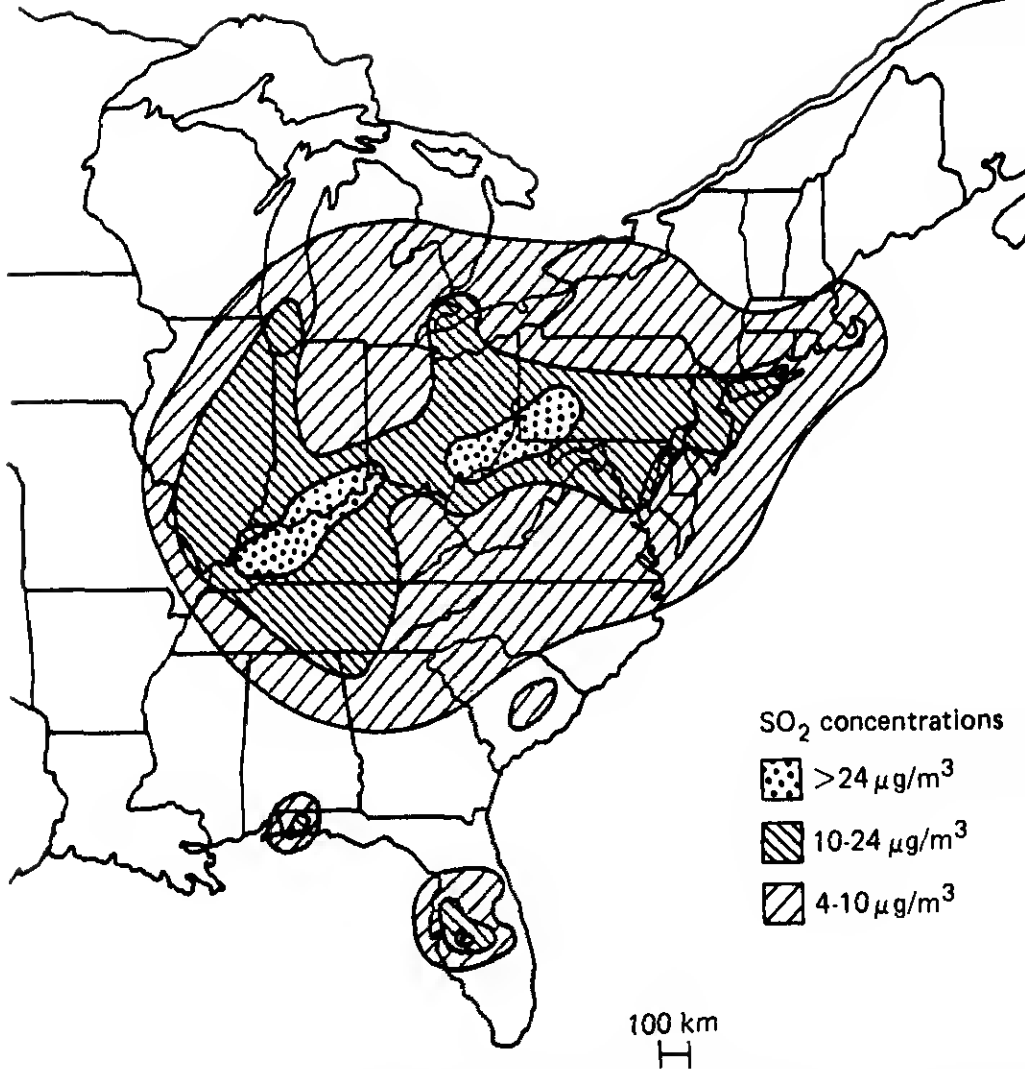
FIGURE 12.14 July 1974 average SO_2 concentrations due to 283 large SO_2 emission sources as calculated by the BN trajectory model.

Another important quantity is the distance of influence (i. e-folding distance or "distance-constant") of SO_2 as a function location of source. This distance of influence is computed as

influence due to source location.

Figures 12.15 and 12.16 show the sulfate concentration and distance of influence as a function of source location. The distance of influence of sulfate ranges from about 250 to 750 km, decreasing from northwest to northeast and southeast. Before trying to interpret these results in terms of meteorology, it is important to note that these distances are probably strongly influenced by edge effects; i.e., trajectories that leave the perimeter of the grid no longer contribute to the sums, and thus the more frequently trajectories are lost, the lower the average distance that is computed. There are also minor influences in remote areas due to choice of grid size and the failure to include all emission sources. The distances that are displayed, however, are probably lower bounds to the actual distance of influence characterizing the sources. Thus, it is clear that sulfates are a regional or subcontinental pollutant in terms of their distance of influence.

12.2.2 Average Travel Distance to Receptor

A second series of questions regarding pollutant transport relates to the control of pollutant concentrations in a region of concern. Here, the question is, "How far away, on the average, are the sources of pollutants influencing a given receptor site of interest?" In terms of concentration fields, this distance scale may be computed by adding up the contributions at a receptor from each trajectory reaching the receptor, i.e.,

$$\rho_{ij} = \sum_k r_{ij,k} \, c_{ij,k} \, / \, \sum_k c_{ij,k}$$

where $c_{ij,k}$ is the concentration at receptor site ij due to all modeled emission sources. Results are shown in Figs. 12.17 and 12.18 for SO_2 and $SO_4^=$ for the array of sources described in the previous section.

For SO_2 concentrations, for receptor sites far from sources, the concentration-weighted average distance (ρ_{SO_2}) to sources is quite large. On the contrary, for receptor sites located close to major sources, (e.g., Illinois, Kentucky, Tennessee, Florida), the influence of these local sources dominates this average. For sulfates, there are regions where local sources dominate (e.g., Illinois and Florida), as well as those in which long-range transport dominates. What is perhaps most interesting is to examine locations such as Boston, Massachusetts where the SO_2 is rather "local" ($\rho_{SO_2} = 200$ km) but $SO_4^=$ is longer range ($\rho_{SO_4} = 1000$
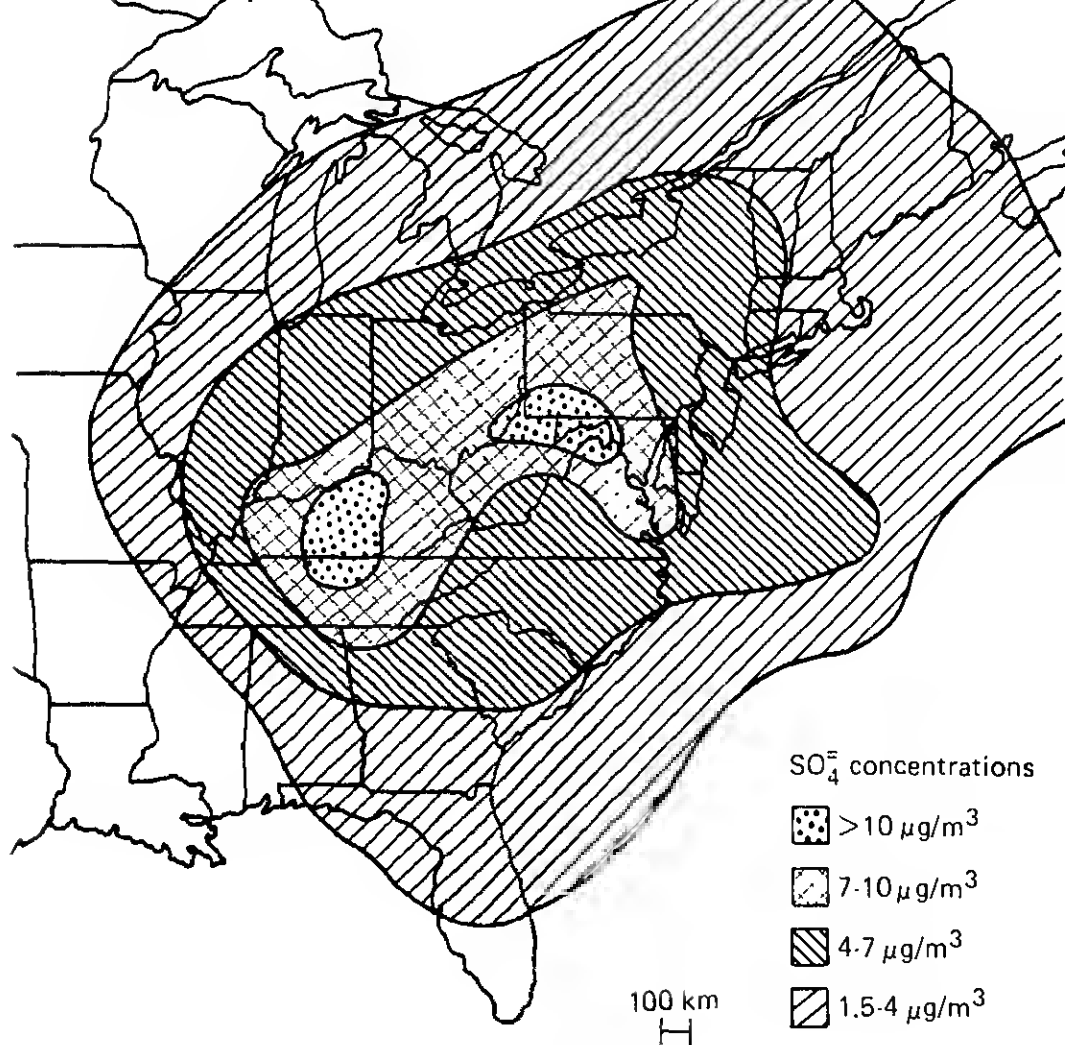
FIGURE 12.15 Same as Fig. 12.14, except for $SO_4^=$.

concentrations, such control would be ineffective to achieve a reduction in $SO_4^=$ concentrations at the same receptor site. Considerations such as these must be taken into account in planning measures to improve air quality.

12.2.3 Back Trajectories for the Study of Acid Rain

The ARL regional scale transport model (Heffter et al., 1975; Heffter and Ferber, 1977) is now being used as an aid to understanding acid rain
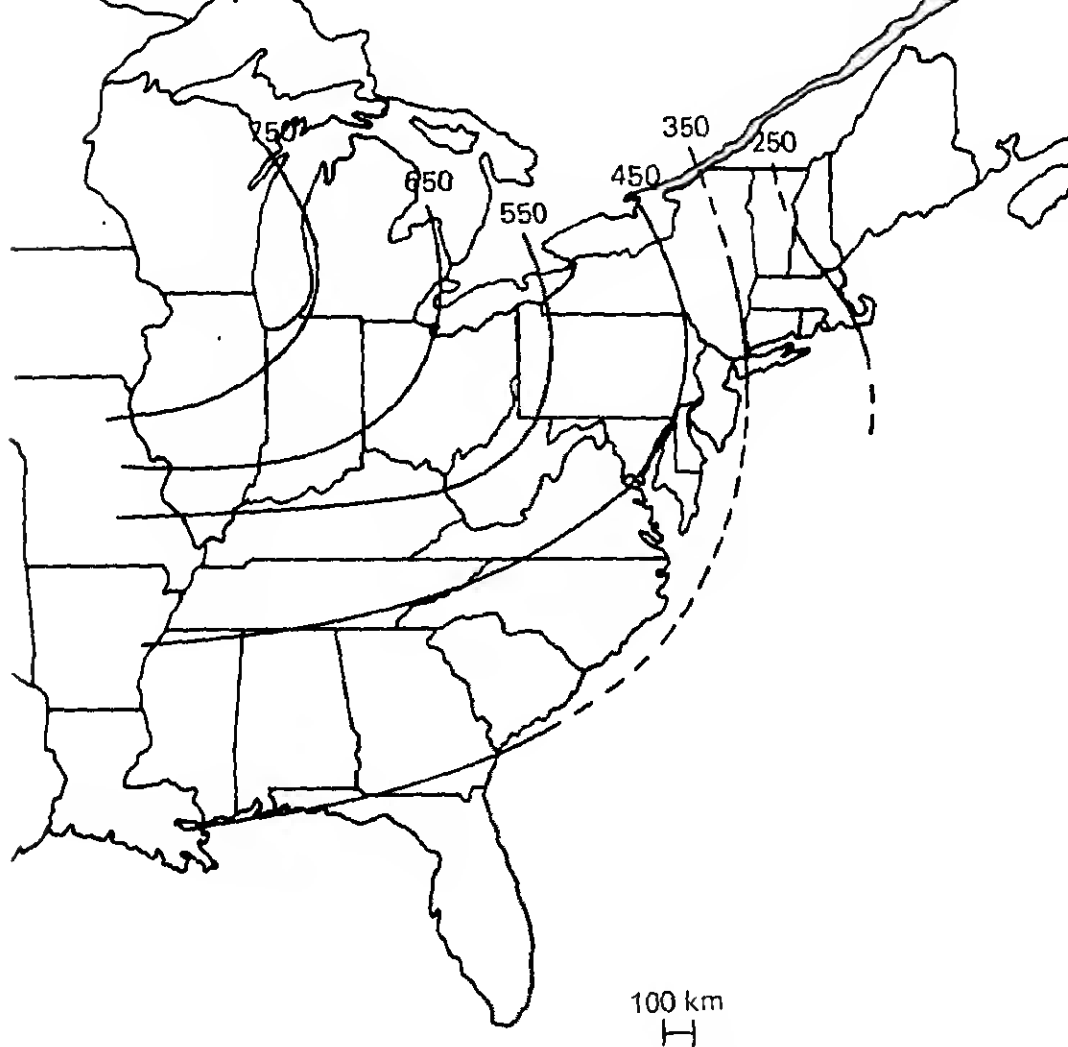
FIGURE 12.16 Distance of influence of $SO_4^=$ as a function of source location (kilometers).

daily at 00Z, 06Z, 12Z, and 18Z, for any desired period such as a month, season, or year. Thus individual acid rain episodes as well as climatological effects can be studied. A transport layer of 600 m to 2000 m above the surface has been chosen for preliminary studies. Multiple layers are also being investigated.

Consideration is being given to how to normalize the specific case
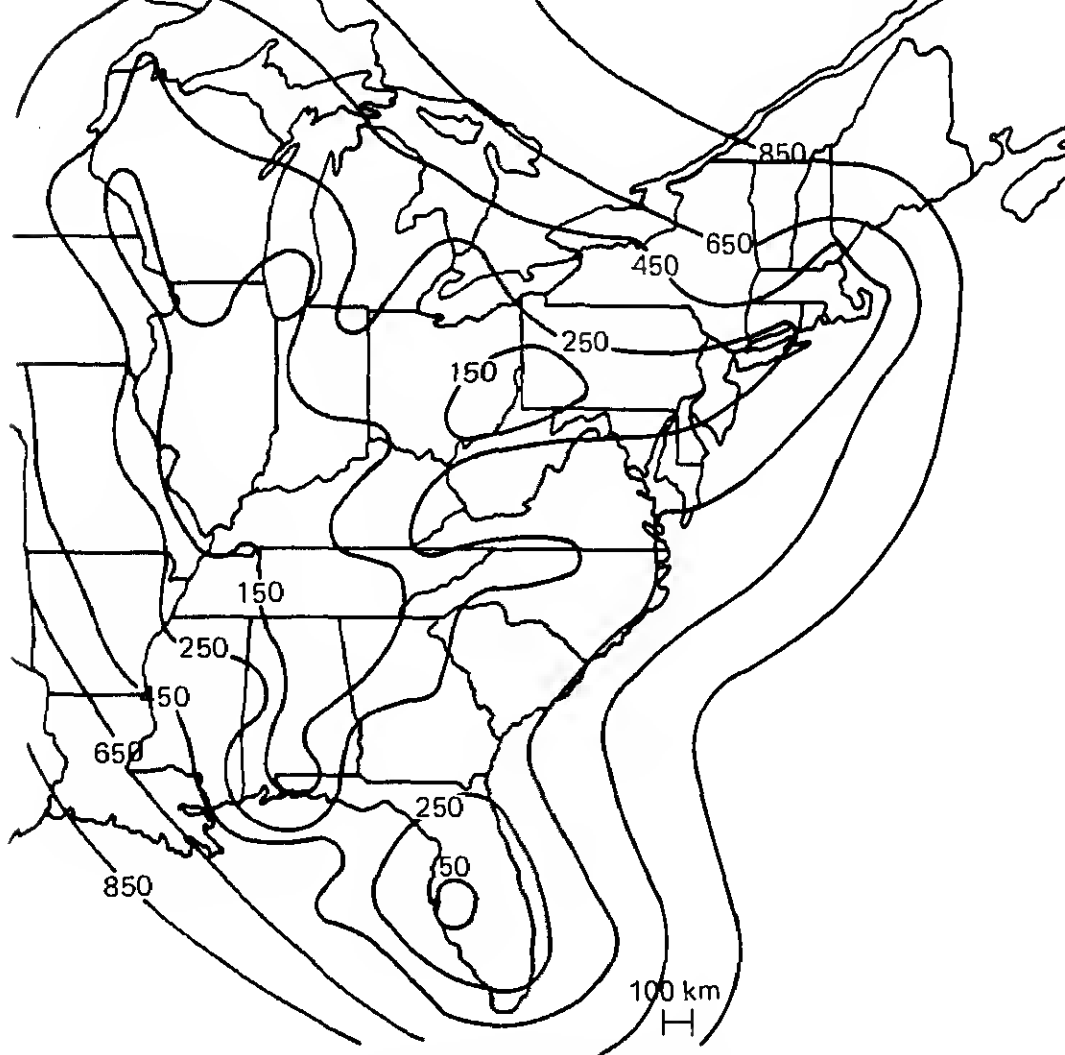
FIGURE 12.17 SO$_2$ concentration–weighted average distance from receptor to emission source (kilometers).

is greatly complicated by the need to consider appropriate three dimensional effects, multiple receptor points, different storm types, etc.

12.3 DEVELOPMENT OF GRID MODELS

While trajectory models allow relatively straightforward calculation
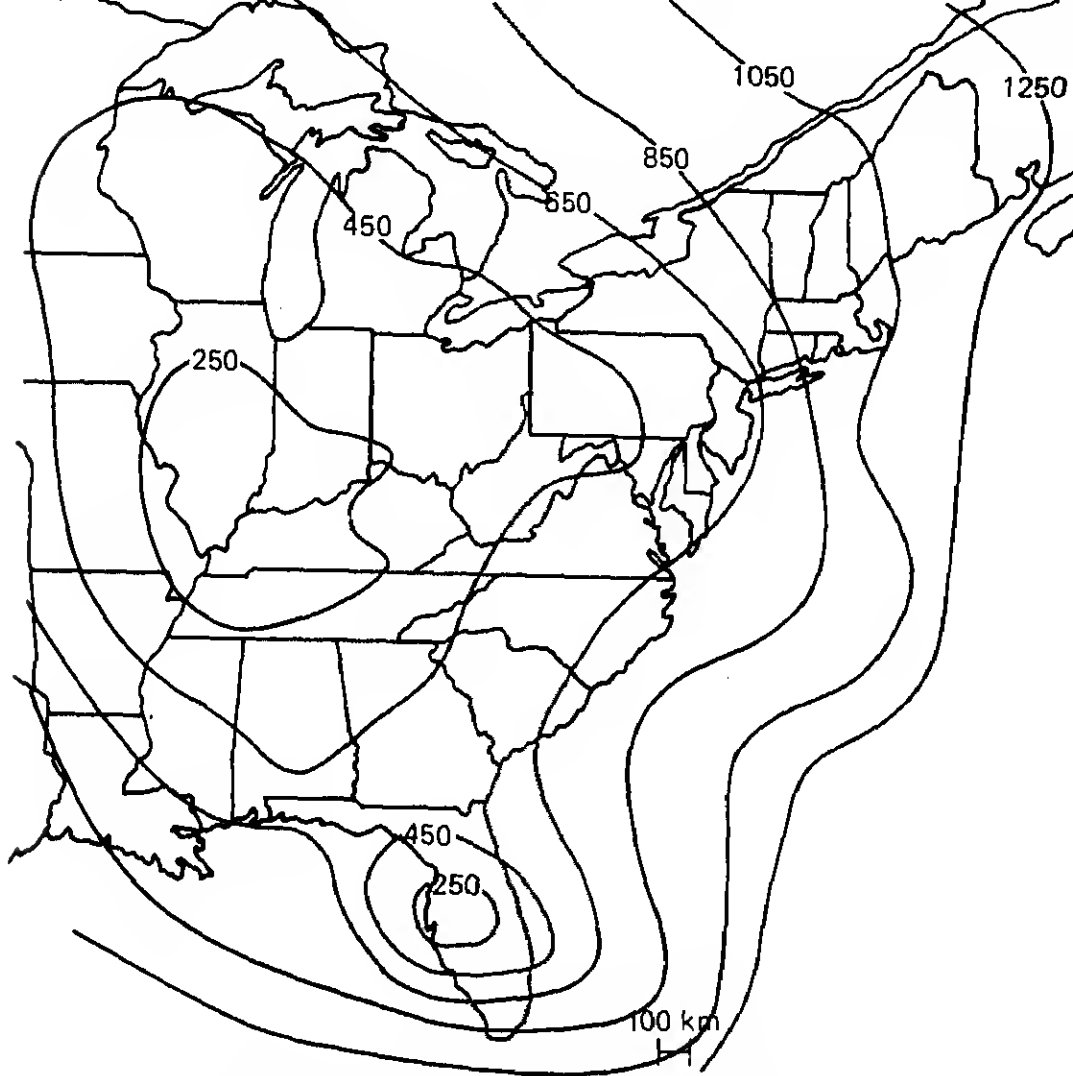
FIGURE 12.18 $SO_4^=$ concentration-weighted average distance from receptor to emission source (kilometers).

sources, when there are many sources, the required calculations become quite extensive. For a very large number of sources, the problem can become nearly intractable. In addition, use of a trajectory approach does not permit (at least in any easy fashion) interaction between plumes and non-linear chemical reactions, thus ruling out treatment of the photochemical processes that may contribute to sulfur dioxide to sulfate

the increased model complexity. These include development of a numerical method that can treat both transport and chemical processes accurately, that can represent multiple vertical layers moving in different directions, and a means of representing dispersion from point sources on a grid with resolution of about 40 km.

MAP3S has supported two approaches to this problem, one with major emphasis on representing transport within about 50 km of the source and boundary layer processes in a manner that permits meshing with a regional model (Section 12.3.1); and a second approach that focuses on developing a model that can treat transport accurately and still simulate atmospheric photochemistry (Section 12.3.2). It is hoped that tne two approaches can ultimately be melded to produce a capability for greatly improved simulation of regional air quality.

12.3.1 The Puff-Grid Model

The six-particle puff model developed by Sheih (1978b) incorporates wind shear and dynamic plume-rise computations in a Gaussian puff. Wind shear increases dispersion of pollutants through differences in wind speed and direction at various levels of the plume. Speed shear can stretch the top of the plume downwind, while directional shear can significantly increase the lateral dispersion of pollutants. The conventional approach in computing plume rise is to use the formulae summarized by Briggs (1970). These formulae are developed under the assumptions of steady state conditions and spatial uniformity; such conditions are frequently absent because of the nocturnal inversion cycle or because of large-scale subsidence inversions. In order to treat these problems a six-particle puff model has been developed. The model simulates a plume from a continuous source with a series of puffs. Each puff is represented by a set of six tracer particles that define the size, shape and location of the puff. Initially, these particles are located at the surface of the source, on arbitrarily chosen orthogonal axes. The location of the particles are computed at each time step by taking into account advection, eddy diffusion, wind shear and entrainment of ambient air during plume rise. The concentration distribution of each puff is determined by fitting an ellipsoid to the cluster of the six particles and assuming a three-dimensional Gaussian distribution, with standard deviations equal to the half lengths of the principal axes of the ellipsoid. The concentration at a point of interest is obtained by summing the contributions from nearby puffs.

The six-particle puff model can be used either to improve the calculation of plume rise, and thus the selection of the proper wind field for trajectory models, or to minimize the problem of insufficient spatial

dilution of the power plant source by a factor of 10^{-8}. The six-particle puff model parameterizes the subgrid-scale pollutant distribution and passes the pollutant puff to the grid system when the dimensions of the puff grow to a size comparable with the grid dimensions.

In conjunction with the development of the puff-grid model, substantial effort has been devoted to development of efficient advection-diffusion schemes that minimize numerical error. The numerical method essentially combines the puff-in-cell method of Sklarew (1970) and the moment method by Egan and Mahoney (1972). Briefly, the method replaces Sklarew's numerous particles in a grid volume by a puff and then approximately conserves moments calculated from Gaussian subgrid-scale distributions, rather than rectangular distributions as in the case of Egan and Mahoney. Detailed descriptions of the numerical methods have been reported by Sheih (1978c) and Shannon (1979).

Furthermore, a combined plume-finite difference mesoscale model for simulating thermal coagulation and dispersion of aerosol particles from an industrial area source has been completed by Sheih (1977c). The model has been used to examine the effect on air quality of filtration of large particles from an emission source. Figure 12.19 shows the concentrations of various particle sizes as function of downstream distance from release for a typical industrial source without air pollution control. Figure 12.20 shows results from a second simulation under exactly the same conditions except that the emission for particles larger than 5 μm is assumed to be zero. Comparison of these results indicates that particles larger than 5 μm effectively remove particles smaller than 0.01 μm and that removal of larger particles from emissions prolongs the residence time of smaller particles.

12.3.2 Eulerian Photochemical Model

Currently there exists no three-dimensional air quality model having properties generally recognized as suitable for representing the overall evolution of pollutant transport while at the same time treating the nonlinear transformations of chemical species (such as sulfur oxides) associated with the generation of fossil fueled power. The desired properties of an ideal model would include, but not be limited to, regional coverage with relatively fine spatial resolution, numerical methods that can treat "stiff"[*] sets of equations with low numerical diffusivity, high speed of computation with a requirement of only small active storage, capability to treat a large number of sources and active

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[*]"Stiff" sets of equations are characterized by having an unusually wide
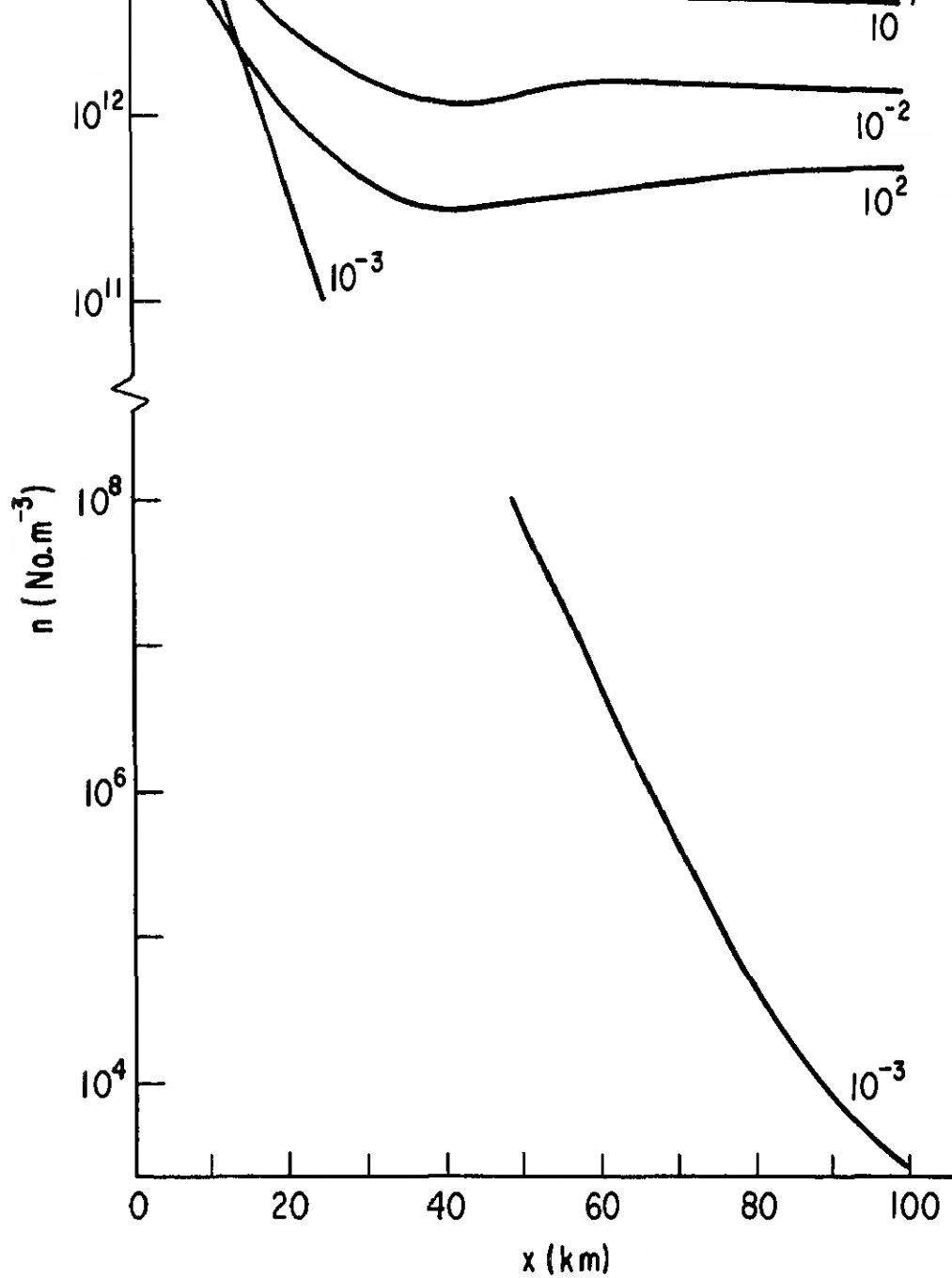
FIGURE 12.19 Particle concentration by particle size as a function
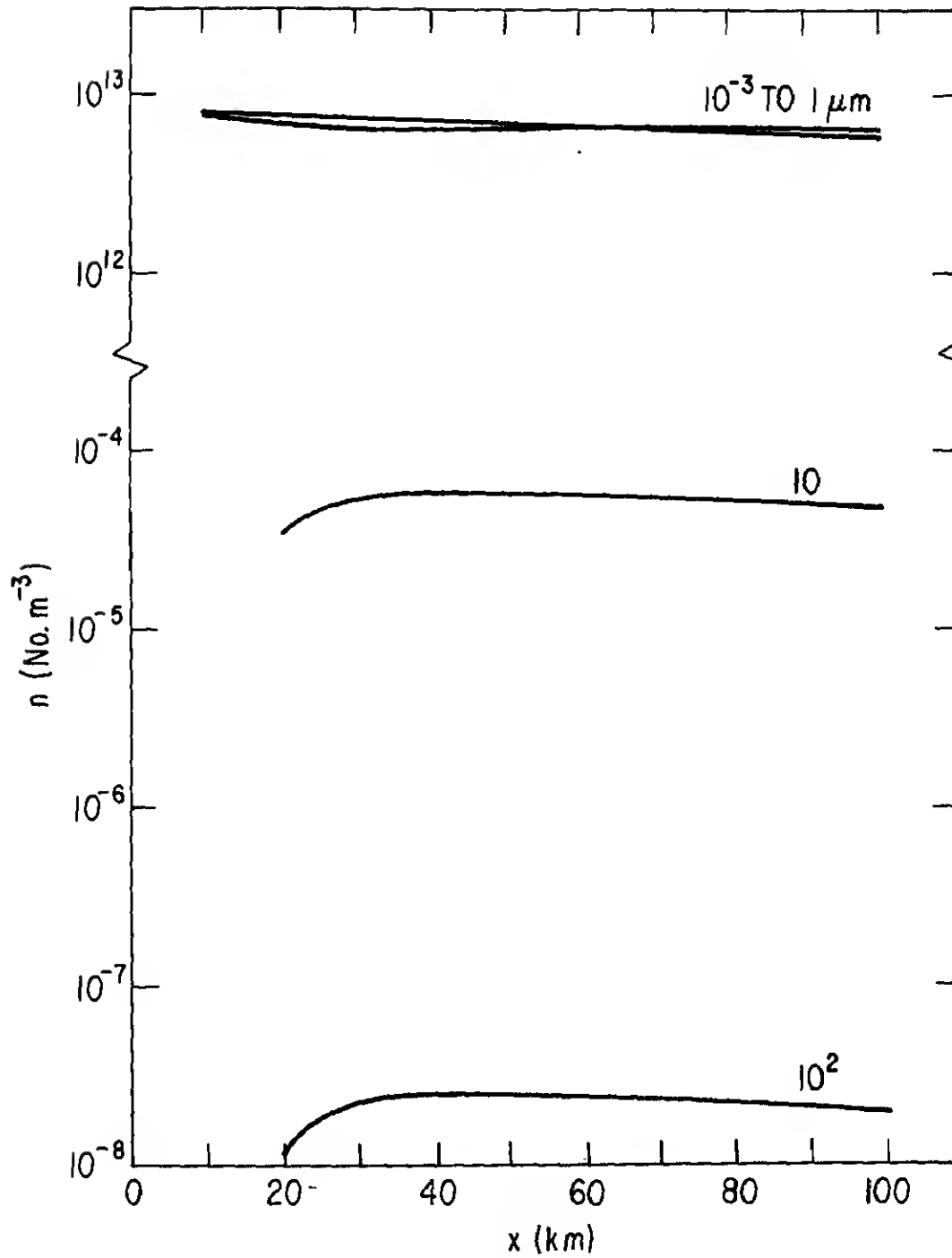
must be made in implementation of these ideas by, for example, treating some reactions as if in pseudo-steady state and developing a special means to handle sub-grid scale effects in a representative fashion.

The initial effort has been to choose or develop a suitable numerical method since this has been a problem in similar models designed to represent urban air quality. A spectral method has been developed that is at least as accurate as that of Prahm (Prahm and Christensen, 1977) but, unlike Prahm's method, is suitable for direct and concurrent computation of the nonlinear stiff chemistry. This method may be compared with several existing methods in the following manner. The method has significantly better advection properties than that of MacCracken et al. (1978), an advanced transport-photochemical model applied to the San Francisco Bay Area; however, MacCracken's method is completely positive and conserving in mass while the spectral method is designed to have negligible mass loss and negativeness. In the spectral model, space derivatives are expressed as double Fourier transforms. This results in replacing the space derivatives with a sum of concentrations and coefficients at grid points. Many of these coefficients are negligible, i.e., the coefficients affect the solution by less than a factor of 10^{-10} and can be dropped completely from the calculation. The resultant method therefore has infinite order resolution (as the number of grid points goes infinite), can be made faster than previous Fourier transform methods, and can be used in conjunction with nonlinear stiff chemistry systems using explicit or implicit solution methods. The calculations are performed completely in real space as opposed to Fourier spectral space.

To provide a test of the double spectral transform method, the ordinary differential equations were solved using the ordinary differential equation system solution code EPISODE (Hindmarsh, 1975). The cone advection test (Molenkamp, 1968; Long and Pepper, 1976; Prahm and Christensen, 1977) was applied and results were nearly identical to those of Prahm and Christensen using the fast Fourier transform method, although their method would not be suitable for direct coupling of nonlinear chemistry. Times for computation were compared using the full set of orthogonal coefficients and using the approximate sparse set. For one revolution of the cone, with the full coefficient set, the computation time using EPISODE was 30 minutes, at this stage much slower than Prahm.

The multi-grid procedure (see below) has been applied in conjunction with a stiff system solver as an integral part of the process. This has resulted in an increase in speed with the added bonus of increased

in representing the long waves) and wherein the finer grid can be used to obtain a correction on the coarse grid solution. Ideally, the fine grid terms tend to be local in nature, and can therefore be solved locally, again promoting efficiency in both storage and time. In concept, many telescoped grid levels can be used in large problems.

Using the implicit double transform spectral method, the method progresses somewhat as follows. On the coarsest grid, using coarse initial conditions, a coarse solution for one Δt is obtained using a couple of iterations of a predictor-corrector method. The coarse solution (level 1) is then interpolated to a grid, having one-half the grid spacing of the coarse grid (level 2). An equation for the error difference between the coarse grid solution interpolated to fine grid and the fine grid solution can be written. This error is, in principle, high frequency in space. Again this equation is subjected to the predictor-corrector procedure. The purpose of the iterations is to utilize the smoothing properties of the predictor-corrector relaxation to smooth the errors and purge the high frequency components, thereby allowing the coarse grid to be applied again with increased efficiency.

In the cone advection test four levels were used. This resulted in increased speed compared to the EPISODE solution, the run time going from 30 minutes to 30 seconds. The solution method, in addition to being faster is also more accurate. To test this further, a short confirmatory test was devised (Lee and Meyers, 1979). A poor, low-order, fully implicit numerical scheme was substituted for the spectral method, and a comparison was made for accuracy using the same five grid resolution as previously published results (Long and Pepper, 1976). Indeed, it was found that the accuracy of the multi-grid cone solution did not decay nearly as quickly as with Long's solution method. This suggests that some lower order methods might be coupled with multi-grid even when high order accuracy is needed.

The multi-grid technique has several further advantages. Variable grids may be used, even with the spectral method. Further, the grids may be stored so that, with little loss of efficiency, active storage in the computer is proportional to the natural logarithm of the number of grid points in the spatial domain. Thus active computer storage space for many large grid applications may diminish as a problem.

With the method now selected and proven, work is proceeding on comparing results from a two-dimensional version of the model with results from a trajectory model. Subsequent to that development and verification of the model is planned.

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CHAPTER 13. MAP3S SPECIAL ACTIVITIES

To encourage progress on the overall program and to provide assistance to specific program elements, MAP3S has undertaken a number of special activities. These activities have been intended to make the scientific community more aware of MAP3S and related research through participation in meetings and assembly and dissemination of data gathered or needed by MAP3S researchers. Efforts by others to participate in MAP3S activities have also been supported, especially as consultants to various groups, but also simply as visitors at MAP3S meetings.

13.1 MAP3S DATA BANK

13.1.1 MAP3S Index of Experiments

To facilitate the flow of information about the MAP3S program to other interested researchers, a computerized data base has been designed to serve as an index to the experiments that have been or will be carried out with MAP3S support. An initial report form was designed and distributed to all program participants. Responses were computerized and a first draft report form was created. This report form, in turn, was sent to the appropriate researcher for comments and corrections.

The current version of the data base is kept on line for MAP3S participants to scan. This data base is also used by MAP3S Data Management personnel as the repository of information pertaining to the data on file at the MAP3S Data Bank. A list of the field programs now included in the index of experiments is given in Table 13.1.

Future work in this area includes a possible revision of the report form and the development of additional reports as user needs indicate.

13.1.2 MAP3S Data Bank

In addition to listing the actual experiments, a data bank has been created to store and make available the many observations being taken as part of MAP3S. The data bank also archives data from other sources needed by MAP3S researchers (see Section 13.1.3).

For archiving MAP3S data, the use of the proposed ANSI* standard for an Information Interchange Data Descriptive File as the format for

TABLE 13.1 MAP3S Index of Experiments

Experiment Code	Experiment Title	Investigator Name	Scope of Experiment
ANL-7712-1	O(18) enrichment of atmos. SO_4, SO_2, precip H_2O and SO_4 in precipitation	B. D. Holt, R. Kumar P. T. Cunningham	Pollutant transformation of atmospheric $SO_4^=$ and components analy... for O(18) content compared to O(... content of standard mean ocean ... Variations in O(18) provide inform... tion on mechanisms for conversio... SO_2 to $SO_4^=$.
ANL-7801-1	Sulfate, acid sulfate, and nitrate content of atmos. aerosols	S. A. Johnson, R. Kumar, P. T. Cunningham	IR analysis of time resolved parti... from Stage 4 of a Lundgren impac... Emphasis placed on the detection ... acid sulfate, but quantity of nitra... neutral sulfate in the aerosol is a... determined.
ANL-7805-1	Turbidity experimental network	M. L. Wesely	Weather, climate modification m... ment of extent of regional episod... increased haze and assessment of ... associated changes in solar radiat...
ANL-7810-1	First diagnostic atmospheric cross-section experiment (DACSE-1)	D. Sisterson	Examine meteorological and air q... structure and daily PBL evolution... a vertical slice up the Ohio Valley... Meteorological data consist of ... five daily rawinsonde soundings.

TABLE 13.1 Continued.

Experiment Title	Investigator Name	Scope of Experiment
Northport plume study	R. W. Garber	Measure SO_2 and $SO_4^=$ species in the plume to characterize the sulfur chemistry occurring there.
Horiscope (horizontal scoping experiment)	S. Schwartz	Determine horizontal/temporal uniformity/variability of SO_2 and $SO_4^=$ concentration to serve as input to design of subsequent studies. Obtain side-by-side comparison of aircraft and tower filter sampling nephelometer.
MAP3S August characterization studies (airborne studies)	R. W. Garber	Characterize the ambient pollution in the NE U.S.
AMBIENS	R. W. Garber	Attempt box budget experiment.
	R. L. Tanner	Characterization of gaseous and particulate S, N compounds at or near ground level in the greater N. Y. area in conjunction with MAP3S/SURE/NYSAS ground and airborne experiments.
Vertical characterization studies	R. W. Garber, R. M. Brown, G. J. Ferber	Observe vertical distribution of pollutants in the atmosphere near a large metropolitan area.

TABLE 13.1 Continued.

Experiment Code	Experiment Title	Investigator Name	Scope of Experiment
OAA–7805–1	Field test of new atmospheric tracers (Idaho)	G. J. Ferber	Test release, sampling (to 90 km), analysis for perfluorocarbon tracers and heavy methanes. Simultaneous release with SF_6. Test performance of 3 type perfluorocarbon samplers, measure tracer concentration at and 90 km from release.
NL–7609–1	MAP3S precipitation chemistry network	M. T. Dana	Characterize the chemistry of precipitation in the NE U.S. by precipitation sampling and rapid analyses for all major ionic species. Provide model with chemistry data for individual storms, study trends in fossil fuel pollution.
NL–7805–1	Transformation in urban plumes	A. J. Alkezweeny	To determine the transformation of SO_2 and SO_4 and to identify the oxidation mechanisms. The experiments are performed using 2 instrumented aircraft.
NL–7806–1	Precipitation scavenging	B. Scott	To identify major removal and transformation mechanisms associated with the wet removal of SO_4.

TABLE 13.1 Continued.

Experiment Code	Experiment Title	Investigator Name	Scope of Experiment
NL-7806-2	AMBIENS	J. M. Hales	To define input and output fluxes, temporal and spatial variability of pollutant over a 100 km squared gr... element.
NL-7806-3	MAP3S/SURE Intensive	J. M. Hales	Regional aircraft measurements.

submitted by MAP3S program participants is stored and is available for distribution within and outside the MAP3S community subject only to a few limitations specified by the researcher in charge. Requests for data both for MAP3S participants and non-MAP3S participants are now being processed; a cost recovery fee is charged for non-MAP3S participant requests.

A listing of data now available in the MAP3S Data Bank is given in Table 13.2.

13.1.3 Data Exchange with SURE Program

Procedures have been established for data exchange between the MAP3S and the SURE program. Data formats for SURE data input to the MAP3S Data Bank have been established and SURE ground station data are being received as ERT releases it. Requests from MAP3S participants for SURE data and initial SURE requests for MAP3S data are being processed.

Future work in this area includes further testing and possible revision of procedures and data formats for exchange of data and refinement of the internal handling of data requests.

TABLE 13.2. Data Available in MAP3S Data Bank

1. PNL Precipitation Chemistry Network Data - 9/22/76 to 6/30/78.

2. ANL AMBIENS/COSPEC Data - SO_2, Meloy 185 Sulfur, Meloy 285 Sulfur - October 4-13, 1977.

3. ANL DACSE-I Data - pressure, height, temperature, dew point, wind speed and direction - August 1-10, 1977.

4. ANL Sulfate Acidity Data - Lundgren impactor data - $SO_4^=$, NH_4^+, NO_3^-, $H^+/SO_4^=$, HC - February-November 1977.

5. ERT/SURE Ground Station Data for August 1977 to December 1977. SO_2, NO_x, NO, O_3, temperature, dew point, TSP, $SO_4^=$, NO_3^-, filter sampler.

6. Characterization of gaseous and particulate sulfur and nitrogen compounds at or near ground level in the greater New York Area - BNL Station - July, August 1977. Wind speed and direction, RH, temperature, solar radiation, particle counts, $SO_4^=$, SO_2, NO_3^-, NH_4^+, strong acid.

combine the display of the MAP3S precipitation chemistry data and NOAA precipitation data using mapping and graphical techniques.

13.2 THE BNL-NMC COMPUTER LINK

To assist in prompt analysis of MAP3S field experiments and to assist in model verification and application, MAP3S has established a real-time data link between the computers at the National Meteorological Center (NMC) at Suitland, Maryland, and BNL so that routinely available weather information can be received at BNL. Planning is underway to use data available from this link to examine the applicability of MAP3S models to meteorological air quality forecasts and to impact assessments and data analysis. Data may also be available rapidly enough to conduct timely post analysis of field experiments, and perhaps to assist in operational control of field projects. Because the BNL computer is available to MAP3S participants, they will be involved, to the degree possible, in cooperative meteorological investigations using the BNL-NMC meteorological link.

The combination of a real-time data connection to NMC, coupled through a versatile communication computer (PDP 11/70), in turn connected to a 4th-generation computer system (two CDC 6600's and one CDC 7600), gives the system unique capabilities in the model applications and development area. For example, observational meteorological data can be received from Suitland and then can be edited and displayed on the PDP 11/70 before being sent to the CDC 7600. On the 7600, the data can be combined with source inventory data, thus permitting meteorological and air quality models to be run. The model results could then be sent back over the communication lines to NWS for independent verification, or be disseminated to other locations. Thus, the BNL-NMC link can be used for advanced model (see Chapter 7.4) application and verification.

The available computer hardware that has been installed is listed in Table 13.3. Software development is also proceeding, including the capability for data transfer from NMC, statistics and graphics routines, and plotting routines for trajectory forecasts. Currently, the system routinely receives meteorological data from North America and vicinity. Expansion of area coverage is planned. Software development is still needed to archive and process data received into formats suitable for model runs.

Future plans for interfacing models to the data base include the

Capability	Date Installed
PDP 11/70 computer	September 1977
DEC RSX-11M (version 3) operating system	September 1977
NMC data link	September 1977
BNL 7600/6600 data link	September 1977
DEC disk cartridges (portable)	November 1977
Gould printer/plotter	June 1978
Multiplexer for remote access	August 1978
DEC disk	September 1978
Kennedy tape drive	September 1978

- BNL trajectory model using upper air observations (Chapter 7.3).

- Kreitzberg Mesoscale Model (Chapter 7.4).

- BNL AIRSOX (SO_x air quality) model using gridded forecast fields (Chapter 12.2).

By running models using forecast data, forecasts of air quality may ultimately be available. Future plans also include the use of data to interface with various routines that provide enhanced analysis of the data (a nowcast) such as the variational complex terrain model in BNLMET (Chapter 7.3).

13.3 MAP3S PARTICIPATION IN ISSA

With the recognition in the early 1970's that the U. S. was beginning to suffer ecological effects related to acid precipitation, a number of international meetings were held to encourage exchange of information with European scientists who had been addressing the problem for many years. In the area of atmospheric sciences, a need was recognized to combine the expertise of American scientists in terms of understanding processes controlling atmospheric concentrations with the European expertise in long range transport and deposition. Spurred by the efforts of Prof. Rudolf Husar of Washington University, the Department of Energy joined with the Environmental Protection Agency, the Electric Power Research Institute, the American Meteorological Society, the United Nations Environmental Programme and the Yugoslav Academy of Sciences to arrange and convene the International Symposium on Sulfur in the Atmosphere (ISSA). The ISSA steering committee was formed to

around the world, including the MAP3S Program Director. The Symposium convened in Dubrovnik, Yugoslavia from September 7-14, 1977, and attracted 160 participants from 22 countries. The Symposium program included twelve sessions of invited review papers and six sessions of briefer contributed papers. These formal sessions were followed by three days allocated for workshops devoted to developing a consensus of opinion among the participants on the various aspects of the problem.

There is widespread agreement that ISSA succeeded in providing for both the exchange of current experience and the basis for continued international contact and progress. Progress since that meeting has been accelerating, in large part due to identification in the workshops of crucial research areas and tasks.

MAP3S participation in ISSA, in addition to financial support for publication of the proceedings, included presentation of three review papers and one contributed paper; extensive participation in the workshops by the eight MAP3S-associated researchers who attended; and financial and editorial support for preparation of a UNEP monograph summarizing scientific findings in a semi-technical style.

13.4 MAP3S NEWSLETTER

As a means of providing for communication of MAP3S activities among the many MAP3S research groups and other interested researchers, a series of quarterly newsletters was begun in April 1976. The newsletter has served as a means of communicating such items as:

- initial plans for upcoming activities,

- notification and summaries of meetings of MAP3S researchers that might be of broader interest,

- initial results of field experiments,

- highlights of analyses of observed data, and

- status reports on operation of various sampler systems.

The circulation of this newsletter has grown from about 100 in 1976 to more than 550 when the tenth newsletter was issued for the period October-December 1978. Among the recipients, in addition to interested

scientists in MAP3S meetings involving such topics as precipitation chemistry and numerical modeling. This participation has in turn led to cooperation on a broad scale in a number of important research areas including particularly interaction with complementary programs being conducted by Canada's Atmospheric Environment Service and the Electric Power Research Institute, and the Environmental Protection Agency.

MAP3S was designed with the intent of being flexible and responsive. The overall focus has been on applying available resources to areas where the uncertainties are the largest and the most important. Although these must be somewhat subjective evaluations, it has been reassuring to have other programs follow our lead and often support some of our efforts as we have focused on precipitation chemistry, dry deposition, aerosol characterization, tracer gas utilization and so on.

In this chapter we attempt to provide an evaluation of where uncertainties now appear to be most significant and what research directions we propose to follow in order to address these issues. In some cases, the prospect is not as clear as it may become next year because during the past two years we have initiated measurement and field experiment programs, but have not yet had an opportunity to conduct a thorough analysis, including evaluation in models, of the available data.

The first section of this chapter discusses limitations of our understanding of regional air quality and precipitation chemistry. We are striving to assure that information beyond such general properties as total particulate loading and rainfall acidity is available so that hypotheses about transport, transformation, and deposition mechanisms can be evaluated.

The second section evaluates the state of knowledge of individual processes and identifies those areas where attention is most warranted. Much of our work to date will be useful in addressing present conflicts in understanding of sulfur budgets and cycles, but there is clearly a need now to move particularly into areas that couple precipitation chemistry and air quality by, for example, making in-cloud and near-cloud measurements. Such data will be needed to determine where the hydrogen ions come from, why aerosol and rainfall acidity are so different, and what the relative roles of nitrogen and sulfur oxides are.

The third section reviews the limitations of present models in terms of answering questions related to air quality and precipitation chemistry. These limitations remain large, despite substantial progress in improving the models during the last two years and indications that progress this coming year will be substantial.

14.1 REGIONAL CHARACTERIZATION

14.1.1 Air Quality Characterization

conceived with the aim of providing the data set against which integrated models could be tested. The amount of detail that can be achieved is obviously dependent upon the resources applied; and it is equally true that model verification studies can profitably use as much data as are ever available. A key strategy has been to perform the MAP3S measurements in concert with other programs in order to maximize the utility of the information collected.

The extensive surface and aircraft measurements performed in the SURE program were augmented by MAP3S with detailed aerosol measurements and regional scale aircraft measurements. This has allowed for much greater coverage than either program could have accomplished on its own. However, the necessity to insure that the combined efforts were in phase has meant that the data processing and analysis have lagged behind the field measurements program; efforts are currently underway to begin the very large task of analyzing and interpreting the combined MAP3S-SURE data set, and this will be an item of very high priority in this research area in the next few years.

With the end of the field phase of SURE, a large part of the MAP3S characterization effort will shift from wide area coverage to measurements on a scale that approximates the grid size expected to be used in MAP3S models (about 30 km in the horizontal and through and above the mixed layer in the vertical). There will be particular emphasis on the documentation of spatial and temporal inhomogenieties that require either approximation or parameterization in regional scale models and that could influence sub-grid scale phenomena. Additionally, there is to be further examination of mechanisms that might modify the transport and transformation of pollutants. In particular, better documentation is required on the variation of the vertical distribution of pollutants as a function of time of day and synoptic conditions. Aircraft soundings, primarily aimed at studying the effect of synoptic conditions, will be done on semi-routine basis to document seasonal variations; these will probably be done in the eastern part of the Greater Northeast in order to be able to observe material that has been transported long distances. Some examination of diurnal effects will also be made during these flights; however, a more concentrated effort will be made during the Central Illinois Rainfall Chemistry Experiment (CIRCE), discussed below, in order to take advantage of the concentrations of observations to be made by other MAP3S participants.

In these experiments attempts will be made to obtain profiles using the recently developed continuous sulfate monitor in addition to taking "Hi-Vol" samples at various constant altitudes. Measurements will also

importance of vertical transport, will test the approximations used in models for calculating vertical distributions, and will provide data for model testing.

The framework, grid size, and input meteorological data of models in current use for the regional scale are such that mesoscale flows associated with lake and sea breeze circulations are not treated well, if at all. Data from the New York Summer Aerosol Study (Section 6.1) suggests that significant compositional changes take place when pollutants are recirculated in a sea breeze. The perturbation of trajectories by such circulations will clearly affect transport. It should be noted that sea breezes occur frequently when stagnating high pressure systems, which cause elevated pollutant levels or are part of the synoptic situation that sets up ducting regimes, are over the coastal regions. During several summer characterization flights the effect of sea breezes upon pollutant distributions were observed. A series of coordinated aircraft and surface-based measurements will be made to investigate the effects of such coastal flows. These experiments will seek further to document compositional changes and to provide a basis for more sophisticated calculational methods and parameterizations for use during conditions conducive to lake and sea breeze development.

Urban concentrations will perturb regional scale transport and transformation in a variety of ways. Beyond the fact that urban areas are sources of pollutants, the mix of pollutants can change radically, thereby affecting transformation rate. During such conditions, the air flow can also be modified by the roughness and heat sources of the cities, an event that in turn can affect transformation. In order to document these perturbations, aircraft measurements will be planned to characterize the pollutant mix and concentrations flowing into and out of several urban areas in the east. The data collected will be used to help determine the nature of sub-grid parameterizations required in the vicinity of cities.

14.1.2 Precipitation Quality Characterization

Precipitation-quality research has progressed along two general fronts during the MAP3S program. The first of these fronts is the measurement and monitoring of precipitation quality. Because of the MAP3S effort there now exists a substantial data base of high-quality, event-scale measurement of precipitation chemistry at the four initial MAP3S stations. Data from the present eight station network are also becoming available. These data are expected to be used extensively in future analysis of annual cycling, and spatial distributions, and for general model development and calibration.

addition, continuation of the sampling program during future years will begin to provide necessary information regarding long-term temporal trends - an essential feature in view of the basic objectives of MAP3S.

The MAP3S precipitation-chemistry network is coordinated with the National Atmospheric Deposition Program (NADP) NC-141 network, which is national in scale and began operation during July 1978. The MAP3S network has served as a pilot study for the NADP system; it has provided comparisons of sampler types, sampling methodologies, sampling frequencies, and analytical techniques, all of which are pertinent to the design of the national network. Exchange of data has also been an important element of these activities, with the rapid release of MAP3S data setting a strong precedent. We expect this type of interaction to continue. In addition, the MAP3S work on rain chemistry at the Illinois State Water Survey was instrumental in their selection as the Central Analytical Laboratory of the NADP. Special tests currently in progress regarding SO_2 deposition and the PNL/HASL/CANSAP sampler intercomparison (see Chapter 5.3) are expected to benefit all future networks of this type. Moreover, the fact that the MAP3S system samples on an event basis will allow it to function as a short time-resolution core for the NADP system, which obtains samples with a one-week duration.

This last aspect is particularly important. Granat (1978) has shown that long-term sulfur deposition trends in Europe cannot be evaluated successfully unless the data are analyzed on a storm-by-storm basis, implying a requirement for sampling with an event (or shorter) frequency. By providing a reasonably long run of event-sampling experience it is expected that the MAP3S data base - with informed and judicious interpretation - will be useful in generating trend information and providing input to ecological effects studies.

14.2 FIELD EXPERIMENTS

14.2.1 Introduction
The models developed as the main product of the MAP3S program will be of sufficient variety and complexity that complete experimental verification is likely to be impossible. For example, while it is clear that long-range tracer experiments directly address many of the transport processes involved, it is equally obvious that such studies cannot test the simulation of chemical transformation, precipitation chemistry, or dry deposition. Likewise, extensive case studies of pollutant characteristics and transport are capable of testing some aspects of some models; single

parameterization procedures, collected and arranged in order to address particular matters of interest and to emphasize specific features of the pollution problems of the greater Northeast. The main intent of the experimental programs operated in conjunction with the modeling efforts has been to improve the individual parameterization procedures employed in the modeling process, so that more realistic simulations can be developed and so that the constituent formulations of physical, chemical, and biological processes can be defended and supported by high-quality experimental evidence. Experimental work conducted under MAP3S has largely focused on intensive case-study investigations of particular features of pollutant transport, transformation, and removal. This emphasis will continue.

Monitoring experiments are specifically excluded from consideration here; these experiments are those that are intended to document the long-term characteristics of atmospheric pollutants over the MAP3S region, including such features as the spatial and temporal variability. Network experiments like those conducted in the SURE program are not a major component of MAP3S.

14.2.2 Transport Processes

Investigations of atmospheric transport processes will continue to focus on the two main themes evident in the discussion in earlier chapters. Work on the development of improved tracer techniques, suitable for use over the long distances of interest to MAP3S, has already instilled sufficient confidence that sub-continental scale perfluorocarbon tracer experments are being planned. As an outgrowth of this work (in collaboration with ARL/NOAA), continuous real-time measurement of trace quantities of SF_6, as well as perfluorocarbons, is now possible and has been tested in the STATE and AMBIENS field programs. These advanced tracer capabilities are leading the way to new areas of experimental endeavor. For example, it is intended to investigate such matters as the ducting of air through mountain valleys, the entrapment of pollution in closed circulation patterns along shorelines, and the enhanced dispersion of emissions in a convectively active troposphere.

Experimental studies of the planetary boundary layer have already resulted in evidence supporting the isentropic transport (i.e., along trajectories of constant potential temperature) of pollutants (in DACSE-1) and in the development of better formulations for the depth of the mixed layer. At this time, however, the case of the nocturnal boundary layer remains somewhat of a mystery. Further studies of the nocturnal case will be conducted, largely in collaboration with the Central Illinois Rainfall Chemistry Experiment (CIRCE)* planned for

convective storm development to be undertaken primarily by workers from ISWS, the NOAA National Hurricane and Experimental Meteorology Laboratory, and the University of Virginia.

If suitable aircraft become available, observations of the chemical characteristics of air at the outflow regions of convective cells will be used to evaluate the redistribution of sulfur through the troposphere resulting from this particular mechanism. At this time, it is not clear whether clouds provide a major route for leakage from the mixed layer to the upper troposphere, at which levels residence times are known to be considerably greater than the few days usually associated with sulfur emissions into the lower atmosphere.

During CIRCE, special attention will be given to the nocturnal boundary layer and the matter of low level wind maxima ("jets") which potentially transport material for long distances in relatively undiluting, stratified flow at night. This increased ventilation rate at night is thought to be characteristic of clear-sky summer nights, but the phenomenon is not often observed in routine meteorological observations. It is clearly a matter of some considerable importance in considerations of regional-scale pollutant budgets such as are often evaluated in numerical simulations. Experimental investigations of the problems will focus on the development of methods suitable for interpreting (and extrapolating from) routine surface meteorological observations in conditions conducive to low level jets.

Methods for incorporating surface characteristics in sophisticated numerical models will also continue to be investigated. Field studies will be conducted over different kinds of vegetated surfaces, in order to assist in the parameterization of horizontal and vertical dispersion coefficients, stability regimes, etc.

14.2.3 Transformation Processes

Uncertainties about rates of oxidation of sulfur dioxide emitted into the atmosphere persist. Transformation rates in individual power plant plumes are consistently found to be low, but substantially larger rates have been measured in urban palls. Under the MAP3S program, further field investigations of gas-phase chemical transformations are planned, with the intent of expanding the range of conditions studied. Particular emphasis will be associated with the need to examine the nocturnal case and the characteristically more humid but spatially confined shoreline circulation pattern.

Past investigations of the rate of change with time of the concentrations of various chemical constituents of a particular parcel of

as in the da Vinci project) have been made. But this too leads to questions as to whether the tagging system properly identifies the trajectory followed by the pollutants of interest. Clearly, for example, if indeed transport is isentropic then the use of isobaric tagging systems might be misleading unless experiments are conducted when air temperatures are constant with time. Injection of some unique and readily identifiable gaseous tracer surmounts this difficulty, and it is essentially for this reason that it is intended to capitalize upon the real-time, airborne tracer detection system recently developed by BNL and NOAA/ARL.

The cooperative CIRCE experiment, planned for central Illinois in mid-1979, will provide an opportunity to focus on matters related to convective cells. Experimental philosophies similar to those developed in the METROMEX studies of precipitation scavenging will be used to investigate and compare the chemical constitution of air in the inflow and outflow regions of selected convective cells. Transformation rates within clouds will be evaluated, and related to such matters as the concentration of specific chemical species in cloud water and in precipitation, and the acidity of the falling rain. These measurements are intended to be used in conjunction with existing parametric models to deduce quantities appropriate for characterizing precipitation scavenging in comprehensive regional scale calculations.

14.2.4 Surface Removal Processes

Experimental studies of dry deposition will continue to focus on the parameterization of surface fluxes of sulfur dioxide and sulfate particles to surfaces that are characteristic of the MAP3S region. As in the past, ANL's work will be conducted in close cooperation with the EPA/ESRL. Surfaces to be considered in the experimental program include a range of crops in various stages of growth and water stress, snow, and bare soil. Further experiments over forests and pine plantations will also be conducted. Micrometeorological techniques developed in recent dry deposition experiments will be improved by the utilization of better sensors, as they become available. For use in conjunction with eddy-correlation methods, it is imperative that sufficiently rapid response of the entire chemical detection system (of the order of 1 Hz or faster) be attained. For application in gradient studies, prime emphasis must be associated with the accuracy and resolution of the detection system.

Supporting measurements of the turbulent surface fluxes of common meteorological quantities such as the sensible heat flux and the Reynolds stress will be made in all of these field studies. Analyses of the

incorporated in numerical simulations through the use of deposition velocity "maps", similar to those already obtained at ANL.

Although the prime purpose of these studies is to address the problem of regional-scale sulfur pollution, work on ozone fluxes and on the dry deposition of particulate pollutants in general will continue. This work will be expanded to include other pollutants of interest to MAP3S (such as NO_X, for example) as suitable sensors become available.

14.2.5 Wet Removal Processes

In addition to continuing measurement of regional precipitation quality (see Section 14.1.2), there is a continuing need to develop a more adequate understanding of the scavenging processes responsible for removing contaminants from the air and ultimately leading to the chemical compositions observed in precipitation. Both theoretical predictions arising from past experimentation, and supplemental field observations from the MAP3S precipitation chemistry network, imply a substantial sulfate wet deposition throughout the year with maximum deposition occurring during the summer months.

During the first years of MAP3S simplified submodels of sulfate scavenging have been developed that are amenable to incorporation in regional models, yet are sufficiently realistic to start considering key physical features of storms and the scavenging process. Adjustable parameters of these models have been calibrated for specific storm types based upon detailed field studies of such relatively simple, but still complex, systems such as lake-effect storms.

But considerably more work is necessary if we are to achieve an adequate understanding of scavenging processes in all types of storms. Current plans call for participation in a convective cloud study in central Illinois during the summer of 1979. These warm, convective clouds are expected to be extremely efficient scrubbers of pollutants and are felt to be responsible for much of the summertime maximum in sulfate concentrations in precipitation. Thus these summertime experiments should provide the opportunity to evaluate the ability of convective clouds to scavenge SO_2 and sulfate and to test the hypothesis that sufficient pre-existing sulfate is available to account for observed precipitation water sulfur concentrations.

Additional areas of uncertainty are related to the extent of of in-cloud transformation of SO_2 to $SO_4^=$ and to the causative factors of precipitation acidity (e.g., how important is nitrate?). These questions must be resolved in order to adequately evaluate such issues as the role

complexity of these problems, an adequate experimental plan has not yet been developed to investigate them. High priority is being given to determining procedures for studying these phenomena.

We expect this field work to proceed hand-in-hand with both the characterization and modeling tasks. The scavenging-analysis task is designed to determine the rates and mechanisms leading to the results measured in the characterization task. Conversely the characterization task is important for feeding the scavenging analysis information pertinent for the elucidation of mechanism and development of scavenging submodels. This interactive relationship will become significantly stronger in subsequent years when MAP3S network operations, operating on a special, high intensity basis (sequential sampling for selected storms, etc.), will be executed in major field studies for scavenging model development and calibration.

14.2.6 Integral Pollutant Experiments

The 1977 AMBIENS experiment was intended to be a test bed for future investigations of pollutant behavior over meso-scale distances. In the early planning stages of AMBIENS, strong doubts existed about the experimental capability to measure pollutant concentrations with sufficient accuracy to allow interpretation of differences in concentration reported over distances of the order of 100 km, in background atmospheric conditions. In this sense, AMBIENS was essentially a test of the hypothesis that enough is already known about pollutant transformation, transport, and deposition to permit us to develop a budget over an area of much the same size as in many grid models. The results of the experiment are not yet available, but preliminary indications suggest that changes in SO_2 and $SO_4^=$ concentrations can be detected by single monitoring systems (e.g., one instrumented aircraft), with sufficient accuracy to warrant further analysis, but that system-to-system comparison is unlikely to be fruitful.

Thus, the scope of pollution problems that is within our experimental capability seems to be entirely limited by temporal and spatial coverage that can be achieved with available instrumented aircraft. There is little point, for example, in asking different aircraft to monitor pollutant concentrations entering and leaving any specific area of interest, since differences in concentration are likely to be overwhelmed by differences in sampling, calibration, etc., between the two aircraft. Instead, it would be preferable to compress the area of interest until it is sufficiently small that adequate sampling could be within the scope of one of the available aircraft. Early planning anticipated a hierarchy of experiments building upon the (presumed successful) AMBIENS

CIRCE stands as an example of the kind of cooperative, integrated experiment of pollutant behavior that is feasible under the MAP3S program. As mentioned above, CIRCE is a cooperative study by workers primarily from ISWS, PNL, BNL, and ANL scheduled to take advantage of the presence of an impressive array of meteorological and air chemistry facilities in the Bloomington area of central Illinois during the so-called VIN (for University of Virginia, Illinois State Water Survey, and NOAA National Hurricane and Experimental Meteorology Laboratory) investigation of deep convective cloud development planned for July 1979.

Major integrated experiments are proposed in order to test some of the numerical simulations developed under MAP3S. At the time of this writing, however, it is not clear that technological capabilities are sufficiently advanced to permit long-range investigation of specific species of air pollutants. In consequence, it is possible that experiments of this sort will center around tracer studies, involving an assortment of tracer materials such as those recently developed under MAP3S and cooperating programs.

14.2.7 Weather and Climate Modification
Operations of the MAP3S turbidity network, originally planned for two years, have ceased on schedule, and no further network activity is proposed. Future activity will concentrate on analysis of the mammoth amount of data collected, and on a series of more detailed investigations of the interaction between air pollutants and solar radiation components to be conducted at ANL.

An unheralded role of MAP3S in supporting routine meteorological observations at the participating national laboratories will continue; these observations already form a long record of high-quality data which provide often unique insights into weather patterns at the sites concerned.

14.3 NUMERICAL MODELING AND ANALYSIS

14.3.1 Introduction
During the past two years major progress has been made in modeling air quality in the eastern United States, but major work still needs to be done. When MAP3S began, trajectory models with very simple parameterizations were just beginning to be compared against very limited sets of available observations. In the last two years, a substantial new data base has been gathered for use in model

more attention is being paid to vertical mixing (and lack thereof). Perhaps more important, the field programs and process-oriented model developments have laid the foundation for major improvements in the representation of various processes in the regional models.

Chapters 3 and 4 describe a new emissions data base that has been developed using EPA, FPC and state emission inventories. The data base has had a large number of tests made to identify errors and mistakes, and thus should be the most comprehensive data base yet available for the eastern United States.

Chapter 6 describes some of the efforts that have been made in gathering a data base that will allow much more extensive verification of numerical models. The SURE data base on surface air quality and the MAP3S/SURE aircraft data during episode conditions will permit intensive comparison of model results and data. Even more challenging is the data base on precipitation chemistry, a sink mechanism that modelers are only now even beginning to simulate.

Chapter 7 describes methods that allow the mixing height to be estimated during both daytime convection and night-time stable conditions. The BNLMET offers the potential for major improvements in calculating air parcel trajectories, both in the horizontal since terrain is included and in the vertical since layering and stability are taken into account. Even more exciting, but of longer term importance are the developments of prognostic models. The Kreitzberg model that has been implemented at BNL offers great promise in representing precipitation systems and their scavenging of pollutants.

Transformation of pollutants is becoming better understood, as described in Chapter 8. There has been growing agreement on the rate of homogeneous transformation in power plant and urban plumes. These new rates will be able to be used in trajectory models. A set of chemical reactions that represent photochemical and chemical processes with a limited set of species and reactions that can be used in a grid model.

Advances in representing surface removal processes have been very significant, as described in Chapter 9. Field measurements have led to development of a formulation for dry deposition that is a function of atmospheric stability, surface conditions and other factors. Maps of roughness length and surface type have been developed for the eastern United States, thereby providing the information needed to include this mechanism in regional models.

the relative importance of scavenging of $SO_4^=$ (which appears to be the only mechanism active in winter) and the scavenging of SO_2 and conversion to sulfate, that may also be an important process in summer. There has been essentially no progress, however, in simulation of precipitation chemistry (as opposed to wet deposition), as discussed further in the next section.

Finally, there has been a major improvement in the numerical techniques that can be used in developing a grid model, as described in Chapter 12.

Together, these accomplishments during the past two years have laid the framework for continued advances during the next few years. As indicated in the next section important uncertainties remain, but with properly focused field experiments, progress should continue to improve simulation capabilities.

14.3.2 Remaining Uncertainties

The previous section focused on advances in the capability to represent individual processes. What is not yet clear, however, is whether models incorporating all of these processes will yield results that compare with observations. The verification of present models has focused on comparison of monthly average simulations with rather limited observational data. This is satisfactory in only a very limited sense in that agreement on the average is considerably easier to accomplish than agreement with day-to-day variations. With the SURE data base providing extensive information on daily, and in some cases on a three-hourly, basis, this will be a major area for model study during the next few years.

Of particular interest will be results relating to the sulfur budget in the eastern United States. Results from the precipitation chemistry network indicate that approximately one-third of the total sulfur emitted ends up being deposited in the region through wet processes. There is considerable uncertainty at present whether this deposition results mainly from scavenging of sulfate or whether scavenging of SO_2 (and in-cloud conversion to sulfate) is a major contributor to rain water sulfur. Working with the models to investigate the interaction of the various processes to achieve a balance between the rather large wet deposition, the apparently large dry deposition and the relatively low levels of sulfate should help focus attention on critical uncertainties.

There are also several processes that are not yet well enough understood to be treated by present model formulations. These include heterogeneous conversion processes, in-cloud conversion, pumping of

effects.

In addition to simulation of atmopsheric pollutant concentrations, simulation of precipitation chemistry is a MAP3S objective. In this area, accomplishments have been very limited during the past two years. Although there appears to be a correlation of hydrogen ion with precipitation sulfur, the relationship is apparent mainly in the average rather than for individual storms. In trying to identify the source of the hydrogen ions in the rain, measurements indicate that it cannot be from the sulfate aerosol. Further, it is becoming clear that nitrate plays an important role. Thus, if the MAP3S objective of developing a capability to simulate the effect of altered pollutant emissions on rain chemistry is to be fulfilled, considerably more investigation and modeling will be needed.

14.3.3 Plans for Implementation and Development of Improved Models
The major focuses in the MAP3S modeling task during the next two years will involve three major areas:

- Verification studies, primarily with improved trajectory models incorporating new process parameterizations. The SURE/MAP3S data base will serve as the observational record. Comparisons will be made in terms of air quality concentrations and wet deposition on both day-by-day and monthly average time scales.

- Development of a grid model that can treat regional transport, non-linear transformation and wet/dry removal processes. Verification of the model will likely be initiated towards the end of the next two years.

- Further work to improve parameterizations of such processes as precipitation scavenging and vertical shear and dispersion. Adequate representation of precipitation chemistry will likely require substantially more sophisticated treatment of in-cloud conversion, scavenging of aerosols, and the nitrate cycle.

The foundations for substantial progress have been laid; building an adequate structure with the tools available will be a substantial challenge requiring coordinated efforts of the several groups involved.

AGENCY, PROGRAM AND OTHER ABBREVIATIONS

AEC   - Atomic Energy Commission (now DOE)

AER   - Atmospheric Energy-Related (pollutants)

AGL   - Above Ground Level

AMBIENS - Atmospheric Mass Balance of Industrially Emitted an
           Natural Sulfur (October, 1977)

ANL   - Argonne National Laboratory (B. Hicks, P. Cunningham*)

ARAC   - Atmospheric Release Advisory Capability (M. Dickerso
           LLL)

ARL   - (NOAA) Air Resources Laboratory (G. Ferber)

ASEV   - Assistant Secretary for Environment (DOE)

BNL   - Brookhaven National Laboratory (P. Michael)

BYU   - Brigham Young University (D. Eatough)

CANSAP   - Canadian Network for Sampling Precipitation

CAP   - Chicago Area Program (R. Semonin, ISWS)

CIRCE   - Central Illinois Rainfall Chemistry Experiment

CCN   - Cloud Condensation Nuclei

DACSE-I - Diagnostic Atmospheric Cross-Section Experime
           (August 1977)

DBER   - Division of Biomedical and Environmental Research (n
           OHER), DOE (D. Ballantine)

DD   - Distilled, deionized (water)

DOE   - Department of Energy

ML	- Environmental Measurements Laboratory (P. Krey)
PA	- Environmental Protection Agency
PRI	- Electric Power Research Institute (R. Perhac)
RDA	- Energy Research and Development Administration (predecessor to DOE)
RT	- Environmental Research and Technology, Inc. (G. Hidy)
SEERCo	- Empire State Electric Energy Research Corporation
SRL	- Environmental Sciences Research Laboratory (EPA)
EA	- Federal Energy Administration
PC	- Federal Power Commission
ASL	- Health and Safety Laboratory (now named EML)
C	- Ion Chromatograph
N	- Ice Nuclei
SC	- Interstate Sanitation Commission
SSA	- International Symposium on Sulfur in the Atmosphere (R. Husar, Washington University)
SWS	- Illinois State Water Survey (R. Semonin)
ASL	- Los Alamos Scientific Laboratory
BL	- Lawrence Berkeley Laboratory (T. Novakov)
CL	- Lifting Condensation Level
LL	- Lawrence Livermore Laboratory (M. MacCracken)
MAP3S	- Multistate Atmospheric Power Production Pollution Study (M. MacCracken)

METROMEX - Metropolitan Meteorological Experiment (R. Semonin

	mation Program (W. Wilson, EPA)
MMDWC	- Monthly Mean Deposition-Weighted Concentrations
MRI	- Meteorology Research, Incorporated (D. Blumenthal)
NAAQS	- National Ambient Air Quality Standards
NADP	- National Atmospheric Deposition Program (J. Gibs CSU)
NASN	- National Air Surveillance Network (EPA)
NC-141	- National Atmospheric Deposition Program (USDA No Central Region Project Number 141)
NCUA	- National Coal Utilization Assessment (J. Hoover, ANL)
NEDS	- National Emission Data System (EPA)
NMC	- National Meteorological Center
NOAA	- National Oceanic and Atmospheric Administration
NRC	- National Research Council
NSF	- National Science Foundation
NWS	- National Weather Service
NYSAS	- New York Summer Aerosol Study (R. Tanner, BNL)
NYU	- New York University
OHER	- Office of Health and Environmental Research, DOE
PBL	- Planetary Boundary Layer
PEPE	- Persistent Elevated Pollution Episodes (W. Wilson, EPA)
PNL	- (Battelle) Pacific Northwest Laboratory (R. Dra J. Hales)
PSU	- Pennyslvania State University (R. dePena)

R-I	- Rockport, Indiana
RTI	- Research Triangle Institute (J. Worth)
SCORE	- Summer Chemistry of Rain Experiment (R. Semonin)
STATE	- Sulfur Transport and Transformation Experiment (W. Wilson, EPA)
SUNYA	- State University of New York at Albany (R. Falconer)
SURE	- Sulfur Regional Experiment (G. Hidy, ERT)
TCM	- Tetrachloromercurate
UOV	- University of Virginia (J. Galloway)
URl	- University of Rhode Island
USDA	- U. S. Department of Agriculture
VIN	- University of Virginia, ISWS, NOAA National Hurricane and Experimental Meteorology Laboratory summer 1979 field experiment (R. Semonin, ISWS)
VISTTA	- Visibility and Interstate Sulfur Transformation and Transport in the Atmosphere (W. Wilson, EPA)
WSU	- Washington State University (D. Adams)
XRF	- X-ray fluorescence

The following list of researchers who have participated in MAP3S is intended both to make easier the task of contacting particular individuals and, more importantly, to recognize and acknowledge their dedicated efforts on the scientific research described in this report. In many cases MAP3S is a full-time pursuit; in other cases MAP3S research is an augmentation of other, often-related, research already being pursued. The list is arranged alphabetically by organization and provides both commercial and FTS telephone number (if available). Consultants that have provided significant input are included in the list for the organization for which they have consulted (their names are asterisked; separate addresses are not given but their normal telephone numbers are provided).

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APPENDIX C

MAP3S ANNOTATED BIBLIOGRAPHY

The listing of articles and reports in this appendix is organized by chapter according to primary subject matter of the publication. Although not all of the work described in these articles has been supported wholly by MAP3S, these publications are the result of research activities of MAP3S researchers as part of MAP3S and related projects at their laboratories or institutions. In most cases, the particular work cited is the most recent or most complete description of the research; preliminary reports and presentations are generally omitted. Because MAP3S provides only limited support for many of the university groups involved in MAP3S, most have listed only a few of their publications. Copies of most of these reports and articles are available from the authors (their addresses are given in Appendix B).

CHAPTER 2: INTRODUCTION

MacCracken, M. C., "The Multi-state Atmospheric Power Production Pollution Study: Program Plan," U. S. Department of Energy, DOE/EV-0008/1, January 1978.

> The goal of MAP3S is to develop and demonstrate an improved, verified capability of numerically simulating the present conditions and potential changes in pollutant concentration, atmospheric behavior, and precipitation chemistry that result, or will result, from pollutants released to the atmosphere by large-scale power production processes (primarily those that use coal combustion). Results from the MAP3S program will form the basis for answering two critical questions relating to energy and environmental planning:
>
> • Will precipitation acidity and atmospheric turbidity in the United States increase as coal combustion increases?
>
> • Can atmospheric concentrations of particulate sulfur be reduced by decreasing sulfur oxide emissions?

MacCracken, M. C., "The Multi-state Atmospheric Power Production Pollution Study: Addendum: Project Listings for FY-1977," U. S. Deoartment of Energy, DOE/EV-0008/2. January 1978.

Taken together, these research projects and those related activities sponsored by the U.S. Environmental Protection Agency, the Electric Power Research Institute and other organizations, are expected to provide the needed basis for an improved assessment of the impact of emissions of atmospheric energy-related (AER) pollutants from fossil fuel energy generation.

MacCracken, M. C., "The Multi-state Atmospheric Power Production Pollution Program," Proceedings of the Second National Conference on the Interagency Energy/Environment R&D Program, Washington, D. C., June 1977 (also available as Lawrence Livermore Laboratory Report UCRL-79447).

The Multi-state Atmospheric Power Production Pollution Study (MAP3S) is a major atmospheric research program of ERDA's Division of Biomedical and Environmental Research. The MAP3S program is one of several environmental programs being pursued under the Assistant Administrator for Environment and Safety, the activities of which were described in the First National Conference on the Interagency Energy/Environment R&D Program by Dr. James Liverman. MAP3S will ultimately provide improved capability to such programs as ERDA's National Coal Utilization Assessment, which is using present technical capabilities to assess the impact of future coal use.

MacCracken, M. C., "MAP3S: An Investigation of Atmospheric, Energy Related Pollutants in the Northeastern United States," Atmos. Environ., 12, 649-659, 1978 (also presented at the International Symposium on Sulfur in the Atmosphere, Dubrovnik, Yugoslavia, September 1977).

The Multi-state Atmospheric Power Production Pollution Study (MAP3S) is a major new atmospheric research program of the U.S. Energy Research and Development Administration. The goal of the MAP3S program is to develop and demonstrate an improved, verified capability to simulate the present and potential future changes in pollutant concentration, atmospheric behavior and precipitation chemistry as a result of pollutant releases to the atmosphere from large-scale power production processes, primarily coal combustion. Research projects are underway to measure present sulfur oxide concentrations and composition, to assess the potential for long range transport, to investigate transformation processes in plumes from point and urban sources, to sample precipitation chemistry and improve understanding of

Proceedings of the Special Technical Meeting on Atmospheric Sulfates, Philadelphia, PA, Air Pollution Control Association, 1978 (also available at Lawrence Livermore Laboratory Report UCRL-80428).

MAP3S is focusing attention on the answering of the two critical questions:

- Will the acidity of precipitation and atmospheric turbidity increase in the United States with increased coal combustion?

- Can atmospheric concentrations of particulate sulfur be reduced by reducing sulfur oxide emissions?

Research projects are underway to measure present sulfur oxide concentrations and composition, to assess the potential for long range transport, to investigate transformation processes in plumes from point and urban sources, to sample precipitation chemistry and improve understanding of scavenging mechanisms, and to develop numerical models that can simulate future air quality on sub-continental scales given patterns of anticipated combustion emissions.

CHAPTER 3: POWER PRODUCTION EMISSIONS

Benkovitz, C. M., "Compiling a Multistate Emissions Inventory," presented at the Special Conference on Emission Inventories and Factors, APCA-TP7 Committee, Anaheim, CA, November 1978, Brookhaven National Laboratory Report BNL-25043.

This paper describes the development of the MAP3S source emissions inventory projects. Topics covered include the acquisition of both emissions and ancillary data, techniques developed for quality assurance and data updating as well as descriptions of current and future plans in both upgrading and using the inventory.

Benkovitz, C. M. and V. A. Evans, "User Access to the Source Emissions Inventory," MAP3S memo, July 1978.

This memo gives specific user instructions on direct access to the emissions inventory computerized data bases and summary information obtained from the data.

The recommended procedure for flue gas sulfuric acid determination was the controlled condensation procedure. A caution was issued that the IPA methodology could cause significant acid measurement errors and that the techniques employing IPA could not be used at H_2SO_4 concentrations less than 1 ppm.

Dietz, R. N. and R. W. Garber, "Power Plant Flue Gas and Plume Sampling Studies." (a) Progress Report No. 2 (in preparation); (b) Progress Report No. 1, November 1977, Brookhaven National Laboratory.

These reports present the application of the Brookhaven-designed controlled condensation system to the determination of the effects of operating parameters on the formation and emission of sulfuric acid, metal sulfates, and total particulates. Furnace O_2, power level, and fuel oil sulfur and vanadium content each had direct effects on the formation of H_2SO_4. Increasing magnesium oxide additive and flue gas soot levels each had a diminishing effect on H_2SO_4. A correlation was developed that can predict sulfuric acid emissions with a reliability of $\pm 25\%$.

Dietz, R. N. and R. F. Wieser, "Sulfate Emissions from Fossil Fueled Combustion Sources," Semi-annual progress reports through October 1978, Brookhaven National Laboratory.

These reports document the development and validation of methodology for sampling power plant flue gases for sulfuric acid and metal sulfates. Of the two principal methods, the controlled condensation system utilizing the Brookhaven designed in situ nozzle and particulate filter assembly gave the most reliable acid and metal sulfate measurements. Errors were associated with the other method.

Dietz, R. N., R. F. Wieser, and L. Newman, "An Evaluation of a Modified Method 6 Flue Gas Sampling Procedure," in Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources, EPA-600/9-78-020a, August 1978, pp. 3-25.

It was conclusively demonstrated that the utilization of an isopropyl alcohol (IPA) midget bubbler for the collection of sulfuric acid can lead to 2- to 4-fold errors in total sulfate determinations because of positive biases from residual dissolved SO_2, oxidant in the IPA, and oxidant in the flue gas which

Affecting Sulfate Emissions from Oil-Fired Power Units," in *Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources*, EPA-600/9-78-020b, August 1978, pp. 239-270.

In addition to covering most of the work described in Dietz and Garber (1977), detailed analyses of the particulate fraction in the flue gas showed that the soluble portion was composed entirely of water soluble metal sulfates - principally of Mg, V, and Na. Carbon was the main element in the insoluble fraction which also contained metal oxides primarily of Mg, V, and iron. It was also shown that even at units burning oil containing high sulfur (2.5% S) and high vanadium (400 ppm V), sulfuric acid could be maintained at about 1 ppm by maintaining furnace oxygen below 0.1% and metal sulfate emissions less than 2 ppm by maintaining ESP efficiency greater than 90%.

CHAPTER 4: NON-POWER PRODUCTION EMISSIONS

Benkovitz, C. M., "Compiling a Multistate Emissions Inventory," presented at the Special Conference on Emission Inventories and Factors, APCA-TP7 Committee, Anaheim, CA, November 1978, Brookhaven National Laboratory Report BNL-25043.

This paper describes the development of the MAP3S source emissions inventory projects. Topics covered include the acquisition of both emissions and ancillary data, techniques developed for quality assurance and data updating as well as descriptions of current and future plans in both upgrading and using the inventory.

Benkovitz, C. M. and V. A. Evans, "User Access to the Source Emissions Inventory," MAP3S memo, July 1978.

This memo gives specific user instructions on direct access to the emissions inventory computerized data bases and summary information obtained from the data.

CHAPTER 5: MEASURING POLLUTANTS AND THEIR PROPERTIES

Cunningham, P. T. and S. A. Johnson, "Spectroscopic Observations of Acid Sulfate in Atmospheric Particulate Samples," *Science*, *191*, 77-79, 1976.

acidic nature of the particles is observed at all times of the day and may persist for several days in urban areas.

Cunningham, P. T., S. A. Johnson, and R. T. Yang, "Variations in Chemistry of Airborne Particulate Material with Particle Size and Time," Environ. Sci. and Tech., 8, 131, 1974.

Samples of airborne particulate material are classified with respect to particle size and time during their collection by inertial impaction. Infrared spectroscopic analysis is used to measure the major chemical constituents of the samples, revealing that ammonium sulfate is the major compound present in the submicrometer diameter particles.

Hercher, M., W. Mueller, S. Klainer, R. F. Adamowicz, R. E. Meyers and S. E. Schwartz, "An Efficient Intracavity Laser Raman Spectrometer," Appl. Spectroscopy, 32(3), 1978.

The design of an optimized intracavity laser Raman spectrometer is described, and representative Raman scattering data are presented. An intracavity laser power of 160 W was attained with an argon ion laser whose normal output power was 1 W. This technique appears attractive for the determination of trace constituents in the air.

Leaderer, B. P., D. M. Bernstein, J. M. Daisey, M. T. Kleinman, T. J. Kneip, E. O. Knutson, M. Lippmann, P. J. Lioy, K. A. Rahn, D. Sinclair, R. L. Tanner and G. T. Wolff, "Summary of the New York Summer Aerosol Study (NYSAS)," J. Air Pollu. Control Assoc., 28, 321, 1978.

During July and August, 1976, participants from seven research laboratories undertook a collaborative study of the New York City aerosol. The study was designed to characterize both the chemical and physical properties of the upwind or background aerosol and the aerosol in New York City in the summer. This report presents in brief summary form a description of the New York Summer Aerosol Study (NYSAS) and the principal findings that have emerged to date.

Lundgren, D. A., F. S. Harris, Jr., W. H. Marlow, M. Lippman, W. E. Clark, and M. D. Durham (editors), Aerosol Measurement, University of Florida Press, Gainesville, 1979.

Methods and Standards for Environmental Measurement, W. H. Kirckhoff (ed.), National Bureau of Standards Special Publication 464 (U. S. Government Printing Office, Washington, D. C.), 1977.

Discusses the environmental determinants of aerosol electrical diffusion charging as they relate to aerosol size distribution measurements.

Marlow, W. H., "Optical-Size Particle Penetration Through a Diffusion Processor for Filter Sampling," presented at the American Industrial Hygiene Conference, New Orleans, LA, May 23-27, 1977.

Presentation of measured penetrations of 0.3, 0.6 and 2.0 μm monodisperse particles at flows of 3.5 l.p.m. to 35 l.p.m. passing through a one inch Collimated Hole Structure as used in diffusion processor measurements.

Marlow, W. H., "Unipolar Aerosol Diffusion Charging. I: Introduction and Charging of High and Low Dielectric Constant Monodisperse Aerosols by Time-Invariant Ion Distributions," J. Colloid Interface Sci., 3, 543, 1978.

Ion polydispersity is included in unipolar aerosol charging equations; conventional $N_0 t$ (N_0 = total ionic density, t = time) parameterization for aerosol charging is shown not to be unique and is replaced by a Ct (C = conductivity) parameterization useful for slip-flow and continuum-flow particle charging; model calculations illustrating sensitivity of aerosol charging to environmentally realistic cluster ion distributions are performed.

Marlow, W. H., "Unipolar Aerosol Diffusion Charging. II: Ion and Aerosol Polydispersities in Unipolar Charging; the 'Diffusion Charging Mobility Analysis' Hypothesis," J. Colloid Interface Sci., 64(3), 549, 1978.

Macroscopically realizable (i.e., experimentally possible) aerosol charging conditions are discussed; unipolar, polydisperse aerosol charging by polydisperse cluster ions is calculated under several conditions including those applicable to the EAA as a test of the "diffusion charging mobility analysis hypothesis;" implications for EAA performance are given.

Marlow, W. H. (ed.), Aerosol Microphysics. I: Particle Interactions, Topics in Current Physics series by Springer-Verlag (Heidelberg

First of a pair of books treating topics in the physics underlying aerosol and fine particle behavior; chapters on kinetic theory and aerosol transport, accommodation coefficients, inelastic photon scattering, and aerosol interaction forces.

Marlow, W. H. (ed.), Aerosol Microphysics. II: Chemical Physics of Microparticles, topics in Current Physics series by Springer-Verlag (Heidelberg, late 1979 or 1980).

Chapters on aerosol thermodynamics, molecular dynamic Monte Carlo methods in nucleation theory, electronic properties of surfaces and small particles, microparticle microphysics.

Marlow, W. H., "Survey of Aerosol Interaction Forces," to appear in Aerosol Microphysics. I: Particle Interactions, 1979 (tentative).

Discussion of kinetic theoretic (or gas-phase) influences on aerosol motion vs. physical interaction forces for a particle near another particle or surface; general physical forces on particles; first review of modern developments in van der Waals forces applicable to aerosols.

Marlow, W. H. and R. W. Garber, "A New Airborne Aerosol Sampling System," presented at the 71st Annual Meeting of the Air Pollution Control Association, Houston, TX, June 25-30, 1978.

The MAP3S Islander Aircraft-based aerosol sampling system is described.

Newman, L., "Sulfur Chemistry of Atmospheric Aerosols," invited presentation at the Gordon Research Conference on Chemistry at Interfaces, Meriden, N. H., July 1977.

The relationship of the composition of atmospheric aerosols to atmospheric chemistry is discussed. A case is made for the need to develop new and better techniques for determining the chemical composition of aerosols.

Newman, L., "Techniques for Determining the Chemical Composition of Aerosol Sulfur Compounds," Atmos. Environ., 12, 113, 1978. Plenary paper at the International Symposium of Sulfur in the Atmosphere, Dubrovnik, Yugoslavia, September 1977. Published in Sulfur in the Atmosphere, Pergamon Press, 1979.

An extensive critical review is given of the methods presently

Precipitation Sampler," Brookhaven National Laboratory Report BNL-50818, 1978.

This report contains a detailed description of the automatic sequential precipitation sampler designed and constructed at BNL. The report describes materials, dimensions and wiring diagrams. Previous precipitation collectors are reviewed and justification for the BNL design explained.

Raynor, G. S. and J. P. McNeil, "An Automatic Sequential Precipitation Sampler," Atmos. Environ., 13, 149-155, 1979.

This paper is a shortened version of Report BNL-50818. It describes the sampler in less detail and omits some dimensions and most wiring diagrams.

Rosen, H., A. D. A. Hansen, R. L. Dod, and T. Novakov, "Application of the Optical Absorption Technique to the Characterization of the Carbonaceous Component of Ambient and Source Particulate Samples," presented at the 4th Joint Conference on Sensing of Environmental Pollutants, New Orleans, LA, November 1977, Lawrence Berkeley Laboratory Report LBL-6844, 1977.

The optical absorption properties of some ambient and source particulate samples have been measured. These results suggest that the absorptivity is due to "graphitic" soot and that a major fraction of the ambient carbonaceous aerosol in the winter and summer episodes investigated is primary in origin.

Rosen, H., A. D. A. Hansen, L. Gundel, and T. Novakov, "Identification of the Optically Absorbing Component in Urban Aerosols," Appl. Opt., 17, 1978 (in press).

A series of experimental results is presented which indicates that the high optical absorptivity of urban aerosols is due to their "graphitic" soot component.

Rosen, H., A. D. A. Hansen, and T. Novakov, "Identification of Primary Particulate Carbon and Sulfate Species by Raman Spectroscopy," presented at the 4th Joint Conference on Sensing of Environmental Pollutants, New Orleans, LA, November 1977; Lawrence Berkeley Laboratory Report LBL-6843, 1977.

The Raman spectra of ambient and source-enriched samples have been obtained. These spectra indicate that "graphitic" soot

a variety of source and ambient particulate samples. These preliminary data may indicate that the absorptivity is due to "graphitic" soot for the samples studied.

anner, R. L., "Continuing Problems in Sampling and Chemical Speciation of Sulfate in Airborne Particles," Paper No. 487, 29th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH, February 27–March 3, 1978.

   A review is given of methods for sampling analysis and speciation of atmospheric sulfur compounds, esecially sulfur oxyanions present in airborne particles. Wet analytical and physical techniques for sulfate are reviewed and continuing sampling problems for aerosol sulfur constituents are discussed. Chemical speciation techniques, size distribution measurements, and prospects for real-time aerosol sulfur techniques are described.

anner, R. L., "Comparison of Acidic Sulfate Data by Extraction and Titration in the New York City Region," First Symposium on Environmental Analytical Chemistry, Provo, UT, June 21–23, 1978.

   Measurements have been made of the strong acid, ammonium, sulfate and nitrate content of aerosol particles for several urban and rural sites in the New York region and compared with sulfuric acid data by solvent extraction. Heterogeneity of aerosol composition was sometimes suggested by the data although mass balances were difficult to obtain among acidic sulfate components.

anner, R. L., R. Cederwall, R. Garber, D. Leahy, W. Marlow, R. Meyers, M. Phillips and L. Newman, "Separation and Analysis of Aerosol Sulfate Species at Ambient Concentrations," Atmos. Environ., 11, 955-966, 1977.

   Sampling and analysis techniques appropriate for the determination of the chemical composition of sulfate in aerosol particles are described. These techniques are applied to the speciation of sulfate in ambient air-borne particles with a time resolution of one hour or less and with size discrimination in the size range below 0.25 μm. Diffusion sampling experiments for size-segregated chemical composition determination indicated that 1/2 of the airborne sulfate is in particles less than 0.3 μm in diameter. Air-mass backward trajectories were calculated and used with the locations of sulfur oxide emission sources to investigate the hourly variations in sulfate measured during

Monitoring of Ambient Levels of Aerosol Sulfate Using a Flame Photometric Detection System," Paper No. 416, Euroanalysis III Conference, Dublin, Ireland, August 20-25, 1978 (in preparation).

   A system is described for measurement of ambient levels of aerosol sulfur (principally sulfate) with a heated denuder to remove SO_2. Discrimination between sulfuric acid and other aerosol sulfur is achieved and correction made for the effects of humidity, barometric pressure and other environmental variables. Ambient data demonstrates sensitivity to as little as 0.5 ppb S.

Tanner, R. L., R. Fajer and J. Gaffney, "Determination of Parts-Per-Billion Concentrations of Aqueous Nitrate by Derivatization Gas Chromatography with Electron Capture Detection," submitted to Anal. Chem., October 1978.

   A modified nitration-GC-ECD method for trace nitrate analysis (LOD = 10 ng/mL) in environmental samples is reported. Electron-capture sensitive nitrating agents are used with trifluoromethanesulfonic acid as catalyst.

Tanner, R. L., J. Forrest and L. Newman, "Determination of Atmospheric Gaseous and Particulate Sulfur Compounds," in Sulfur in the Environment, J. Nriagu (Ed.), John Wiley and Sons, 1978.

   The current status of measurement techniques for gaseous and particulate sulfur species in the atmosphere is reviewed in moderate detail. Both continuous and manual methods for gaseous sulfur compounds are considered. Recently developed particulate sulfur measurement and speciation techniques are stressed.

Tanner, R. L., R. Garber, W. Marlow, B. Leaderer and M. A. Leyko, "Chemical Composition of Sulfate as a Function of Particle Size in New York Summer Aerosol," Annals N. Y. Acad. Sci., in press (1979).

   Samples of airborne particles were collected in New York City in August 1976 and analyzed for strong acid, ammonium and sulfate with impactor and diffusion battery-based sized classification. Correlation of sulfate with strong acid plus ammonium was high in all respirable particle sizes. Fractions of sulfate mass in nuclei and suboptical size ranges were about equal to those reported for rural ambient aerosols.

Tanner, R. L., R. W. Garber and L. Newman, "Speciation of Sulfate in

further developed and validated, using benzaldehyde to selectively remove H_2SO_4 aerosol from non-reactive filters and isopropanol to remove bisulfates in the presence of sulfates. The improved flash volatilization-flame photometric detection system allows precise determination at the 1 ng S level.

Tanner, R. L., W. H. Marlow and L. Newman, "Chemical Composition Correlations of Size-Fractionated Sulfate in New York City Aerosol," Environ. Sci. Tech., 12, in press, 1978.

Aerosol samples collected in New York during August 1976 and February 1977 with high volume and diffusion samplers were analyzed for strong acid, ammonium, sulfate and nitrate. Ammonium-sulfate correlation was exceptionally high in all respirable size fractions with average $NH_4^+/SO_4^=$ molar ratio about 1.5 in summer and about 2 in winter. Diurnal and seasonal variations in sulfate composition were significant.

Tanner, R. L. and L. Newman, "Chemical-Analytical Techniques for Aerosols," in Recent Developments in Aerosol Technology, D. T. Shaw (Ed.), John Wiley and Sons, New York, N.Y., in press, 1978.

Methods for the determination of the chemical composition of sulfate-containing ambient aerosols are briefly reviewed and their use to identify air masses in which the sulfate portion of the aerosol particles is dominated by sulfuric acid and/or its ammonia neutralization products is explained. Examples are given illustrating the utility of this approach in several, varied field experiments.

CHAPTER 6: REGIONAL POLLUTANT DISTRIBUTION

Brown, R. M. and R. W. Garber, "Airborne Measurements of Aerosol and Sulfate Concentration Discontinuities in Vertical and Horizontal Profiles," American Meteorological Society, Proceedings of the Third Symposium on Atmospheric Turbulence and Air Quality, Raleigh, N. C., October, 1976.

Shows a series of measurements of aerosol and gaseous sulfur species as a function of travel time and air mass transformation. Measurements are made in vertical and horizontal dimensions.

Falconer, R. E., "Acid Rain and Precipitation Chemistry at Whiteface

Change (GMCC), Hilo, Hawaii, January 24, 1978.

    Paper describes cloud water collector and some of the results of cloud water collection.

Falconer, R. E. and R. Farrel, "Measurement of pH in Cloud Water and Precipitation at Whiteface Mountain in the Northeast Adirondacks of New York State," ASRC-SUNYA No. 425, Atmospheric Sciences Research Center, The University at Albany, February, 1977.

Hales, J. M. and M. T. Dana, "Regional Scale Deposition of Sulfur Dioxide by Precipitation Scavenging," submitted to Atmos. Environ., 1978.

    Few measurements of sulfur dioxide in precipitation have been available, chiefly due to sampling and preservation difficulties. Dissolved sulfur dioxide can be a significant portion of the total inorganic sulfur in precipitation, however, as recent measurements on a regional network show. During the winter months, dissolved SO_2 can be as much as 25% of the total sulfur on a monthly deposition-weighted average, but the sulfur concentrations in winter are generally only one-tenth those in summer, where very little sulfur dioxide in precipitation is found.

Kadlecek, J. A., T. Fiust, and V. A. Mohnen, "General Composition of Precipitation a Whiteface Mountain," presented at Lake Placid Symposium on Acid Precipitation, May 4-5, 1978 (proceedings being printed).

Michael, P., R. M. Brown, and R. W. Garber, "Comparison of Particulate and Gaseous Material Within and Above the Mixed Layer," Proceedings of the Fourth Symposium on Turbulence Diffusion and Air Pollution, January 1979, Reno, NV., American Meteorological Society, 1979.

    Presents airborne measurements of aerosol, sulfur dioxide and oxide of nitrogen which have been correlated with temperature structure in the atmosphere. Shows that advection of sulfate can take place above mixed layer potentially contributing to long range transport of this material.

Pacific Northwest Laboratory, "The MAP3S Precipitation Chemistry Network: First Periodic Summary Report (September 1976-June 1977)," PNL-2402, October 1977.

    Detailed descriptions of first four sites, equipment procedures,

Pacific Northwest Laboratory, "The MAP3S Precipitation Chemistry Network: Second Periodic Summary Report (July 1977-June 1978)", PNL-2829, January 1979.

      Brief text updates sites and procedures, with data listings for the second year of operation of the MAP3S network.

Raynor, G. S., "Meteorological and Chemical Relationships from Sequential Precipitation Samples," <u>Proceedings of the 70th Annual Meeting of the AIChE</u>, New York, NY, November 13-17, 1977.

      This paper was based on preliminary data from the first seven months of the hourly sequential precipitation sampling program at BNL. The sampler and procedures are briefly described. A relationship is shown between pH and both sulfate concentration in the sample and small particle concentration in the atmosphere. Concentrations of chemical constituents varied seasonally and with precipitation type. Several case studies of changes within events are presented.

Raynor, G. S. and J. V. Hayes, "Experimental Data from Analysis of Sequential Precipitation Samples at Brookhaven National Laboratory," Brookhaven National Laboratory Report BNL-50826, 1978.

      This report describes the methods used in chemical analyses of the hourly sequential precipitation samples collected at Brookhaven and the chemical and meteorological data recorded for each sample. The bulk of the report is a statistical analysis of the relationships between the chemical and meteorological variables for the first year of data.

Ziegler, E. N., "Precipitation Composition: Northeastern United States," in <u>Advances in Environmental Science and Engineering</u>, J. R. Pfafflin and E. N. Ziegler, Eds., Gordon and Breach, Science Publishers, Inc., New York, 1979.

      Precipitation chemistry measurements for the Northeast are reviewed. Relationships between rain composition and regional air quality are explored. Recommendations for future measurement strategies are given.

Hicks, B. B. and M. L. Wesely, "Heat and Momentum Transfer Character-
istics of Adjacent Fields of Soybeans and Maize," in _Proceedings of
the 4th Symposium on Turbulence, Diffusion, and Air Pollution_,
American Meteorological Society, Boston, 496-510, 1979.

Models of regional-scale air pollution developed under the
MAP3S program make use of meteorological data derived from
routine observations reported by the National Weather Service. It
is not immediately clear how to relate these observations over
"good" meteorological sites to the large-scale features of the
planetary boundary layer that are the basis for most
regional-scale models. Accordingly, measurements made as part
of recent studies of the evolution of the planetary boundary layer
(the "Sangamon" experiments conducted by Argonne National
Laboratory) have been used to compare the micrometeorological
behavior of side-by-side fields of soybeans and maize. Although
the maize canopy was much taller and rougher than the soybeans,
daytime eddy fluxes of momentum and sensible heat were not
much greater: about 35% and 10% respectively. Infrared surface
temperatures generally differed by less than $0.4^{\circ}C$, and net
radiation by less than 10%.

Hoffert, M. I. and J. A. Storch, "A Scheme for Computing Surface Fluxes
from Mean Flow," _Boundary-Layer Meteorol._, 1979 (to be published).

A computational scheme is developed for estimating turbulent
surface stress, sensible heat flux and humidity flux from mean
velocity, temperature and humidity at a single height in the
atmospheric surface layer; conditions at this reference level are
presumed to be known from observations or from the evolving
state of a numerical atmospheric circulation model. The method
is based on coupling the Monin-Obukov similarity profiles to a
"force-restore" formulated for the evolution of surface soil
temperature to yield the local values of shear stress, heat flux and
surface temperature. A self-contained formulation is presented
including parameterizations for solar and infrared radiant fluxes
at the surface.

Meyers, R. E., R. T. Cederwall, W. D. Ohmstede, "Modeling Regional
Atmospheric Transport and Diffusion: Some Environmental
Applications," in _Advances in Environmental Sciences and
Engineering_, Gordon and Breach Publishers, 1979.

This paper describes some applications of the modeling of

variational diagnostic meteorological model useful for providing the regional meteorology over complex terrain for input to air quality models.

Meyers, R. E., R. T. Cederwall, W. D. Ohmstede, and W. aufm Kampe, "Transport and Diffusion Using a Diagnostic Mesoscale Model Employing Mass and Total Energy Conservation Constraints," Proceedings of the Third Symposium on Atmospheric Turbulence, Diffusion and Air Quality, American Meteorological Society, Boston, MA, 90-97, 1976.

> A new method is discussed for interpolating observed meteorological data in both space and time for use in meso/regional scale transport, chemical and radioactive transformation, and diffusion models. The method incorporates basic physical constraints into an objective, numerical interpolation scheme for more realistic reconstruction of meteorological fields from irregularly spaced observation points. Examples of reconstructed wind fields, inversion surfaces and mixed layers are presented. The influence of terrain is reflected in the results.

Sisterson, D. L. and P. Frenzen, "Nocturnal Boundary-Layer Wind Maxima and the Problem of Wind Power Assessment," Environ. Sci. Tech., 12, 218-221, 1978.

> High-resolution measurements of wind profiles collected over central Illinois indicate that nocturnal, low-level wind maxima occur more frequently than previously supposed. Since the periodic contributions of these circulations have been neglected, wind power potentially available over the central U.S. has probably been under-estimated, especially in the case of surveys that have used simple, power-law profiles. An alternative method of profile representation appropriate to stability conditions characteristic of nocturnal wind maxima is reviewed, and it is suggested that the strong wind shears associated with these phenomena may present a special hazard to the long rotor blades of large, horizontal axis wind energy conversion systems.

Uthe, E. E. and R. M. Endlich, "Lidar Observations of Aerosol Distributions During the AMBIENS Field Program," in Proceedings of the Fourth Symposium on Turbulence, Diffusion and Air Pollution, January 15-18, 1979, American Meteorological Society, Boston. (Project report with same title also available, SRI Project 6746).

October 1977. The lidar was operated at the surface field site to document the presence of stable layers aloft and to determine the depth of the mixed layer during daytime hours. Derived mixing depths were in good agreement with radiosonde and sodar data.

Yamada, T., "Prediction of the Nocturnal Surface Inversion Height," _J. Appl. Meteoro._, in press, 1979.

A simple prognostic equation for predicting the development of the nocturnal surface inversion height is constructed from the thermal energy equation. The purpose is to provide a simple method to estimate the nocturnal surface inversion heights to augment the prediction of the mixed-layer heights for regional-scale pollutant dispersion models. A significant improvement of the present model over previous simple models is the inclusion of atmospheric cooling due to longwave radiation. Another important difference that considerably simplifies the present model is the adoption of an empirical expression for the potential temperature profile. Predictions agree quite well with results obtained in the Wangara experiment.

CHAPTER 8: POLLUTANT TRANSFORMATION

Alkezweeny, A. J., "Measurement of Aerosol Particles and Trace Gases in METROMEX," _J. Appl. Meteoro._, 17, 609-626, 1978.

Several experiments were conducted in St. Louis during the METROMEX program to determine the properties and formation of aerosol particles. It was found that the average of several distributions obtained during extended periods of time can be approximated by $\Delta N/\Delta D \propto D^{-4}$ for the optical size range. Furthermore, aerosol particles in the plume are growing by coagulation and chemical conversion. The conversion rate of SO_2 to sulfate is about 11% h^{-1} and the sulfate is composed of mixture of an acid and neutralized salt aerosol.

Alkezweeny, A. J., J. A. Young, R. N. Lee, K. M. Busness and J. M. Hales "Transport and Transformation of Pollutant in the Lake Michigan Area," presented at the 4th Joint Conference on Sensing of Environmental Pollutants, New Orleans, LA, November 10, 1977.

A build up of sulfate and ozone has been observed downwind of Milwaukee and Chicago. SO_2 oxidation is dominated by

press, 1979,

A series of experiments were performed that provided further insight into the relationship between plume sulfate and H_2SO_4 formation and plant operating parameters such as excess oxygen, as well as the effect of meteorological conditions upon oxidation rates. In addition, studies were made of particulate ammonium and nitrate formation in the plume and sulfate drop-out beneath the plume.

Forrest, J. and L. Newman, "Silver-110 Microgram Sulfate Analysis for the Short Time Resolution of Ambient Levels of Sulfur Aerosol," Anal. Chem., 49, 1579, 1977.

Atmospheric particulate samples collected on glass fiber and quartz filters are analyzed for total sulfur at the microgram level with [110]Ag tracer, permitting sulfate analyses of <10 μg $SO_4^=$.

Forrest, J. and L. Newman, "Oxidation of Sulfur Dioxide in the Sudbury Smelter Plume," Atmos. Environ., 11, 517, 1977.

The plume data obtained on the extent of oxidation of sulfur dioxide to sulfate from the Sudbury Smelter operation were interpreted as arising from a heterogeneous catalytic pseudo second-order mechanism. The rate of reaction was found to be $0.2 \text{ ppm}^{-1}\text{h}^{-1}$.

Forrest, J. and L. Newman, "Further Studies on the Oxidation of Sulfur Dioxide in Coal-Fired Power Plant Plumes," Atmos. Environ., 11, 465, 1977.

In studies at four coal-fired power plants, the extent of SO_2 oxidation seldom exceeded 5% for distances as far as 70 km and times as long as 200 min, with essentially all of the observed oxidation occurring within the first few kilometers after emission. No distinct correlation was found between the extent of sulfur dioxide conversion with distance, travel time, temperature, relative humidity, time of day or atmospheric stability.

Forrest, J. and L. Newman, "Oxidation of Sulfur Dioxide in Power Plant Plumes," Control and Dispersion of Air Pollutants: Emphasis of NO_x and Particulate Emissions, AIChE Symposium Series No. 175, Vol. 74, p 48, 1978.

isotope ratios.

Forrest, J., L. Newman and S. E. Schwartz, "Discussions: Oxidation of Sulfur Dioxide in the Sudbury Smelter Plume," Atmos. Environ., 12, 2029, 1978.

   Outlines the application of graphical techniques to the treatment of stack plume data as a means of determining the order of the reaction in plume constituents.

Forrest, J., S. E. Schwartz and L. Newman, "Conversion of Sulfur Dioxide to Sulfate During the Da Vinci Flights," Atmos. Environ., 13, 157, 1979.

   Simultaneous measurements of atmospheric particulate sulfate and SO_2 were made during a manned balloon flight over St. Louis County on June 8, 1976. For an eight-hour period of relatively constant sulfate and SO_2 concentrations, processes responsible for concentration changes were examined to set bounds upon the oxidation rate of SO_2.

Forrest, J., R. L. Tanner, D. Spandau, T. D'Ottavio and L. Newman, "Determination of Atmospheric Nitric Acid with NaCl-Impregnated Filters at High Volume Flow Rates," submitted for presentation at the Environmental Chemistry Division, American Chemical Society Meeting, Honolulu, HI, 1979.

   Sodium chloride-impregnated cellulose filters collected nitric acid vapor from ambient atmospheres at efficiencies of ca 90% per filter when placed downstream from pretreated quartz particulate filters in a high-volume sampler. Artifact conversion of NO_2 to nitrate by quartz was negligibly low. Quartz filters that were pre-loaded with ambient particulates lost nitrate when exposed to aerosol H_2SO_4.

Freiberg, J., S. E. Schwartz, "Aqueous Oxidation of SO_2: The Competition Between Diffusion and Reaction in Mixed Phase Reactions," (in preparation) July 1979.

   Develops an approximate treatment to describe the oxidation of SO_2 in a spherical drop of aqueous solution exposed to trace concentrations of SO_2 in air. Previous analyses that have assumed uniform concentrations of reactant species within the drop are shown to be inconsistent with the measured rate data. Develops a

press), 1978.

Oxygen-18 enrichments in precipitation sulfates varied seasonally and in phase with the corresponding enrichments in precipitation water. The ratio of the amplitudes of the enrichment-vs.-time curves indicated isotopic equilibration between SO_2 and atmospheric water prior to oxidation. Oxygen-18 enrichments in aerosol sulfates appeared to vary randomly with season, but averaged about the same as precipitation sulfates.

Holt, B. D., R. Kumar, P. T. Cunningham, M. Bouchard, A. Engelkemeir, S. A. Johnson, E. L. Nielsen, and J. D. Shannon, "Regional ^{18}O Variations in Particulate Sulfate and Water Vapor at Three Sampling Sites about 100 km Apart," Environ. Sci. Tech., 12, 1394-1398, 1978.

Oxygen-18 analyses were made on atmospheric samples of particulate sulfate and water vapor that were collected simultaneously during a six-day period at three sites, spaced 100 km apart. Concerted variations in isotopic and concentration results were observed, demonstrating an apparent regional impact on the quality and quantity of particulate sulfates in the atmosphere. The ^{18}O content of particulate sulfate varied inversely with concentration, indicating that sulfates of heavy loadings differed in origin, and possibly in mechanism of formation, from those of light loadings.

Holt, B. D., R. Kumar and A. G. Engelkemeir, "Interference by Isotopic Exchange in the Determination of ^{18}O in Environmental Sulfur Dioxide," in Proceedings of the Third International Conference on Stable Isotopes, Oak Brook, IL, May 23-26, 1978 (in press).

Two methods of sampling, in the atmosphere and in flue gas, were tested by converting blends of SO_2, varying in ^{18}O enrichment, to sulfate by hydrolysis-oxidation procedures. Comparison of the ^{18}O values for the SO_2 samples and the corresponding sulfate products indicated that isotopic exchange between the collected SO_2 and the absorbing reagents essentially destroyed the isotopic fingerprint of the SO_2 prior to oxidation to sulfate.

Levine, S. Z. and S. E. Schwartz, "Construction of Surrogate CHEmical

of species modeled. A 12-species surrogate model is constructed that accurately reproduces the simulation results of a more complete 30-species model, but with a 5-fold decrease in execution time.

Levine, S. Z. and S. E. Schwartz, "Modeling Homogeneous Oxidation of Atmospheric SO_2 by a Surrogate CHEmical MEchanism (SCHEME)," Brookhaven National Laboratory Report 24383, presented at the 176th National Meeting of the American Chemical Society, Miami Beach, FL, September 1978.

A 12-species surrogate mechanism suitable for incorporation in transport models was developed to model the homogeneous gas phase reactions in the $HC-NO_x-SO_x$ photochemical system, and tested over a broad range of species concentrations against a more complete 30-species model. Agreement between the models was excellent, with departures no greater than 20% at the worst, despite changes in intermediate concentrations of more than two orders of magnitude.

Miller, D. F., A. J. Alkezweeny, J. M. Hales and R. N. Lee, "Ozone Formation Related to Power Plant Emissions," Science, 202, 1186-1189, 1978.

A rather curious and unambiguous event of excess ozone formation downwind of a power plant was analyzed. A kinetics model used to simulate the event indicated that the excess ozone could be reconciled entirely on the basis of excess nitrogen oxides in the polluted air.

Miller, D. F. and A. J. Alkezweeny, "SO_2 Oxidation in Urban Plumes Over Lake Michigan," presented at the New York Academy of Sciences Conference, January 9-12, 1979.

The SO_2 oxidation in the Milwaukee plume has been studied using experimental data and a photochemical smog model. The model predicted the observed parallel formations of O_3 and sulfate downwind of the city. According to the modeling results, OH and RO_2 were responsible for about 80% of the oxidation during the midday period while HO_2 contributed the rest.

Newman, L., "Plume Characteristics," in Proceedings of the Symposium on Aerial Techniques for Environmental Monitoring at the ANS Meeting, Las Vegas, NV, March 1972, pg. 82.

are summarized. The main conclusion is that the overall extent of oxidation was seldom found to exceed 5% over a range of distances up to 50 km.

O'Brien, E. E., R. E. Meyers, and C. M. Benkovitz, "Chemically Reactive Turbulent Plumes," Proceedings of the Third Symposium on Atmospheric Turbulence, Diffusion and Air Quality, American Meteorological Society, Boston, MA, 160-164, 1976.

This paper describes an investigation into the practicality of using a probability density function (pdf) of joint concentrations as the primary dependent variable in a description of turbulent reactive flow. Partial differential equations for the pdf's are formulated and include the processes of random advection, molecular diffusion, and non-linear chemical reaction.

Peache, M. A. (for Environmental Measurements, Inc.), "Sulfur Dioxide Measurements and Mass Flux Calculations in Support of the AMBIENS Field Experiment," Lawrence Livermore Laboratory Report UCRL-13822, 1978.

The main goal of the AMBIENS field study was to determine the mass flow budget of sulfur from natural and industrial sources over distances of 100 kilometers. The EMI field effort was to provide an estimate of the SO_2 mass flux into and out of the study box by using a ground-based Barringer Research correlation spectrometer (COSPEC) to measure vertically integrated values of sulfur dioxide. Because the COSPEC does not have a zero reference, this experiment was to determine the difference between the SO_2 flux into and out of the box rather than measure absolute values. Even this exercise proved to be somewhat difficult because of problems in determining a zero baseline for each day of measurements.

Schwartz, S. E., "Residence Times in Reservoirs Under Non-Steady State Conditions: Application to Atmospheric SO_2 and Aerosol Sulfate," Brookhaven National Laboratory Report BNL-24650, submitted to Tellus, 1978.

Defines mean age, mean transit time and turnover time for materials not in steady state. Applies the considerations developed to atmospheric SO_2 undergoing diurnal modulation in oxidation and dry deposition rates, and to the aerosol sulfur product. Despite strong diurnal modulation, the several residence times do not greatly depart from their steady-state values unless

Schwartz, S. E. and L. Newman, "Processes Limiting the Oxidation of Sulfur Dioxide in Stack Plumes," Environ. Sci. Tech., 12, 67, 1978.

    Examines the competition between dilution and reaction in an expanding stack plume. Delineates the conditions in which quenching may be expected for higher than first order reactions. Reexamines data of BNL study of Northport, N.Y. oil-fired electric generating station and concludes that fall off in oxidation rate may be due either to plume expansion or reagent depletion, e.g., catalyst poisoning by sulfuric acid product.

Schwartz, S. E. and L. Newman, "Processes Limiting the Oxidation of Sulfur Dioxide in Stack Plumes II," presented at the 70th Annual AIChE Meeting, New York, November 1977, Brookhaven National Laboratory Report BNL-24023.

    A somewhat more pedagogical exposition of the treatment of this subject than Schwartz and Newman (1978). Treats as a second example the plume of the Sudbury, Ontario, nickel smelting plant.

Tang, I. N., "Phase Transformation and Growth of Aerosol Particles Composed of Mixed Salts," J. Aerosol Sci., 7, 361-371, 1976.

    Thermodynamical considerations are given to the phase transformation and growth of a mixed-salt particle suspended in moist air. A mathematical expression is derived to relate the equilibrium droplet size to the solution properties of a multicomponent system. It is shown that, at a given relative humidity, the partition between the liquid and solid phases, the chemical form of the solid phase, and the composition of the aqueous solution may be deduced directly from the solubility diagram, provided that water activities are known over the entire concentration range. A graphical method is developed for making incremental extrapolations of water-activity data from dilute solutions up to the two-phase region. Growth curves for the systems H_2O-$NaCl$-$MgCl_2$ and H_2O-H_2SO_4-$(NH_4)_2SO_4$ have been calculated as a function of relative humidity and chemical composition. Depending on humidity and composition, ambient sulfate aerosols may contain $(NH_4)_2SO_4 \cdot 3(NH_4)_2SO_4$), H_2SO_4, or NH_4HSO_4 as the solid phase.

Tang, I. N. and H. R. Munkelwitz, "Aerosol Growth Studies: II. Ammonium Bisulfate Aerosols in a Moist Atmosphere," J. Aerosol

humidity. Monodisperse salt aerosols having a log-normal size distribution with a geometric standard deviation of 1.07-1.13 were prepared and exposed to various relative humidities. Concurrently in separate experiments, measurements were made of the water vapor pressure over aqueous NH_4HSO_4 solutions in the temperature range of 5-25°C for salt concentrations varying from saturation to 11.53% by weight. The data, also reported here, were used in the theoretical growth calculations. Good agreement was obtained between the experimentally measured and the theoretically predicted growth. No size-distribution broadening due to condensational growth was observed. From the growth measurements and vapor pressure data, a relative humidity of 39.0 ± 0.5% was established as the deliquescence point for NH_4HSO_4 aerosols in the optical size range.

Tang, I. N., H. R. Munkelwitz, and J. G. Davis, "Aerosol Growth Studies: II. Preparation and Growth Measurements of Monodisperse Salt Aerosols," _J. Aerosol Sci._, 8, 149-159, 1977.

A continuous-flow apparatus has been developed for studying inorganic salt particle growth by water vapor condensation. Monodisperse salt aerosols in the submicron size range were prepared by nebulizing an aqueous solution, dried, and subsequently size separated using a mobility separator of simple construction. The aerosol extracted from the separator was subjected to various relative humidities, and the equilibrium size changes were measured with an optical counter calibrated for different particle shapes and refractive indices. The system was characterized by measuring the size changes exhibited by a NaCl aerosol at a number of specific relative humidities. The experimental results were compared with those calculated from thermodynamic considerations and good agreement was obtained. At 25°C, airborne NaCl particles were found to transform abruptly into saturated solution droplets at a relative himidity of 75.7 ± 0.4%. This is in good agreement with the reported value of 75.3% measured for the bulk solution. The technique is well suited for measuring the growth of either pure or mixed inorganic salt aerosols.

Tang, I. N., H. R. Munkelwitz, and J. G. Davis, "Aerosol Growth Studies: IV. Phase Transformation of Mixed Salt Aerosols in a Moist Atmosphere," _J. Aerosol Sci._, November 1978.

The phase transformation and subsequent droplet growth of the

aerosol before and after growth by water vapor condensation was continuously monitored with an optical particle counter. It was found that mixed-salt aerosols were characterized by stage-wise growth when the relative humidity in the atmosphere was increased. The onset of growth took place at a specific deliquescence humidity determined by the water activity at the eutonic composition. Thus, mixed NaCl-KCl aerosols deliquesce at $73.8 \pm 0.5\%$ r.h. regardless of initial compositions. For sulfate aerosols containing 0.75 to 0.95 mole fraction $(NH_4)_2SO_4$ (the balance being H_2SO_4), the onset of growth occurs at $69.0 \pm 0.5\%$ r.h. In the composition range of 0.5 to 0.75, a deliquescence humidity of $39.0 \pm 0.5\%$ is noted. Below 0.5 mole fraction, however, the mixed-sulfate aerosols are expected to exhibit hygroscopic properties on the basis of thermodynamic considerations.

Tanner, R. L., J. Forrest and L. Newman, "Determination of Atmospheric Gaseous and Particulate Sulfur Compound," chapter from <u>Sulfur in the Environment: Part I. The Atmospheric Cycle</u>, edited by J. O. Nriagu, John Wiley and Sons, 1978.

Methods are described for instrumental and wet chemical measurement of gaseous and particulate sulfur compounds in the atmosphere. Some applications of sulfur dioxide and sulfate measurements to atmospheric chemistry are reviewed.

Thiemens, M. W. and S. E. Schwartz, "The Fate of HS Radical Under Atmospheric Conditions," presented at the 13th Informal Photochemistry Conference, Clearwater, FL, January 1978.

Establishes that HS radical reacts under atmospheric conditions to form SO_2 with essentially unity yield, rather than forming sulfate directly. HS is the major initial product of atmospheric reaction of H_2S.

Young, J. A., and A. J. Alkezweeny, "Trace Element Concentrations Downwind of Milwaukee and Chicago," presented at the 4th Joint Conference on Sensing of Environmental Pollutants, New Orleans, LA, November 10, 1977.

Size distribution of sulfate and trace metals were determined by a Lundgren impactor. More than 90% of the sulfate was found in particle sizes below 0.3 μm in diameter.

Analysis of Particulate Sulfur and Lead Gradient Data Collected at Argonne National Laboratory," Atmos. Environ., in press, 1979.

Two automatic aerosol particle samplers were operated at heights of 11.5 and 34.5 m on meteorological tower at Argonne National Laboratory (about 40 km southwest of Chicago) during the summer of 1976. Data obtained during one week of intensive study permit evaluation of the horizontal transport of both particulate sulfur and lead; sulfur was found to be associated with southwesterly flow, while lead appeared to originate in Chicago. By combining measurements of particle concentration gradients with wind and temperature gradients, deposition velocities of particulate sulfur have been computed for a range of atmospheric conditions. The resulting evaluations show a strong dependence on atmospheric stability and on wind speed. Although larger than values normally associated with particulate sulfur, the deposition velocities, averaging about 1.4 cm s^{-1}, compare favorably with both the momentum transfer velocity and some recently reported results obtained by application of eddy correlation methods.

Hicks, B. B. and P. S. Liss, "Transfer of SO_2 and Other Reactive Gases Across the Air-Sea Interface," Tellus, 28, 348-354, 1976.

The deposition velocities of soluble and reactive gases above water bodies are nearly linearly dependent upon wind speed and are a function of the prevailing stability regime. In near-neutral conditions, the deposition velocity is about 0.13% of wind speeds at a 10 m height, 0.2% at a 1 m height.

Hicks, B. B. and C. M. Sheih, "Some Observations of Eddy Momentum Fluxes within a Maize Canopy," Boundary Layer Meteoro., 11, 515-519, 1977.

In order to investigate possible routes for pollutant distribution and deposition within a canopy, a series of in-canopy studies were performed during the extensive "Sangamon" field experiment conducted by Argonne National Laboratory during 1976. Vertical momentum fluxes measured by analog covariance equipment and hot-wire anemometers inside a dense canopy of mature maize were found to vary exponentially with height above the ground. The data are well described by the use of an attenuation factor of about four.

Sheih, C. M., M. L. Wesely, and B. B. Hicks, "Estimated Dry Deposition and Sulfur Over the Eastern United States and Surrounding Regions,"

basis of assumed values of surface roughness length, surface resistance to uptake, wind speeds, and stability conditions. Interpretation of a map of land-use types allows application of the methods to various models of pollutant behavior on a regional scale.

Wesely, M. L., J. A. Eastman, D. R. Cook, and B. B. Hicks, "Daytime Variations of Ozone Eddy Fluxes to Maize," Boundary Layer Meteoro., 15, 361-373, 1978.

The vertical flux of ozone to both mature and senescent maize crops has been measured by eddy correlation techniques. For the healthy crop, uptake through stomata accounts for most of the removal of ozone from the atmosphere during the daytime. Surface resistances at the senescent maize field are slightly larger.

Wesely, M. L. and B. B. Hicks, "Some Factors that Affect the Deposition Rates of Sulfur Dioxide and Similar Gases on Vegetation," J. Air Poll. Control Assoc., 27, 1110-1116, 1977.

The deposition of SO_2 and similar gases on vegetation appears to be primarily controlled by diffusion through leaf stomata. The resulting minimum resistance to SO_2 uptake is typically $0.7 \, s \, cm^{-1}$, as indicated by various experimental data. This resistance can become much larger depending on a large number of environmental and physiological factors. The deposition velocity, which consists of the inverse of the sum of aerodynamic and surface resistances, can be computed for a variety of typical situations.

Wesely, M. L. and B. B. Hicks, "Dry Deposition and Emission of Small Particles at the Surface of the Earth," in Proceedings of the 4th Symposium on Turbulence, Diffusion, and Air Pollution, American Meteorological Society, Boston, 510-513, 1979.

Eddy-correlation techniques have been applied to measure deposition velocities of particles $0.05-1.0 \, \mu m$ over a variety of natural surfaces. As measured with the present particle sensor, many surfaces appear to be sources of particulate material at times, but resuspension does not seem the major cause. Over surfaces ranging from grass to forest, the effective surface resistance during downward fluxes is about $1 \, s \, cm^{-1}$. Wintertime bare soil and snow yielded fluxes only directed upwards.

the Atmosphere," Atmos. Environ., 11, 561-563, 1977.

Eddy-correlation measurements of the vertical flux of particles in the size range of 0.05-0.1 μm indicate that the deposition velocity at 5 m above a moderately rough surface varies from 0.1-1.0 cm s^{-1} in light winds. The velocities are only slightly less than the corresponding estimates for momentum and a few gases that are highly reactive at the surface.

CHAPTER 10: WET REMOVAL PROCESSES

Adamowicz, R. F., "A Model for the Reversible Washout of Sulfur Dioxide, Ammonia and Carbon Dioxide from a Polluted Atmosphere and the Production of Sulfates in Raindrops," Atmos. Environ., to be published, 1979.

Illustrative model simulations suggest that the chemical composition of rain is mass-transfer rate limited, carbon dioxide was found to have little effect on the concentration transients or the approach to equilibrium composition of raindrops as they fall through the mixed layer and ammonia considerably increases rain's capacity for sulfur.

Hales, J. M., "Wet Removal of Sulfur Compounds from the Atmosphere," Atmos. Environ., 12, 389-399, 1978.

This paper presents a brief overview of our current capability to calculate sulfur scavenging rates. The general wet removal process can be decomposed into several individual pathways. These include direct sulfur dioxide scavenging, direct sulfate scavenging, and combined scavenging and chemical reaction. Modeling approaches for these pathways are discussed, and pertinent research areas for improvement of our present modeling capability are recommended. At the present time the calculation of direct sulfur dioxide scavenging appears to be well in hand, although more careful network measurements of dissolved sulfur dioxide concentrations in rainwater are needed to establish the relative importance of this phenomenon on a regional scale. Direct sulfate scavenging presents a more difficult calculational problem, and much more data regarding particle-size relationships of sulfate-containing aerosols is required before an adequate understanding of this pathway can be achieved. Sulfur scavenging via the pathway of sulfur dioxide absorption followed by

describing this pathway can be obtained.

Hales, J. M., "Precipitation Chemistry Investigations in the Continental United States," Proceedings of the AIChE National Meeting, Miami Beach, FL, November, 1978

This paper summarizes basic features of past and present large-scale networks in North America, including the NC141, MAP3S, EPA/NOAA, and CANSAP projects. A basic rationale for network design is also given, along with a basic discussion of rain acidity.

Hales, J. M., "How the Air Cleans Itself," Proceedings of the SCI Sulphur Symposium, London, England, May, 1979.

This is a Principal Paper for the deposition session of the Sulphur Symposium. As such it provides an overview of wet- and dry-deposition mechanisms and modeling practices, and summarizes the current and projected states of understanding in these fields.

Hales, J. M., "Wet and Dry Removal of Atmospheric Sulfur Compounds," Proceedings of the SCl Sulphur Symposium, London, England, May, 1979.

This is a more detailed companion paper for the Principal Paper described above. Wet and dry deposition processes are discussed in detail and model-selection algorithms are presented.

Hales, J. M. and M. T. Dana, "Precipitation Scavenging of Urban Pollutants by Convective Storm Systems," J. Appl. Meteoro., to be published in March, 1979.

A precipitation-chemistry network was operated in the St. Louis area in a material-balance study of scavenging of urban pollutants by convective storms. Focusing upon the species SO_2, $SO_4^=$, NO_3^-, NO_2^- and H^+, this study demonstrated that much of the pollutant burden from the city can be scavenged at distances rather close to the source. The study also produced results indicating that aqueous-phase conversion of SO_2 is a significant sulfate-production mechanism, and may account for the observed annual cycling trend of $SO_4^=$ concentration.

Hales, J. M. and M. T. Dana, "Regional Scale Deposition of Sulfur Dioxide by Precipitation Scavenging," Atmos. Environ. in press, 1979.

available, chiefly due to sampling and preservation difficulties. Dissolved sulfur dioxide can be a significant portion of the total inorganic sulfur in precipitation, however, as recent measurements on a regional network show. During the winter months, dissolved SO_2 can be as much as 25% of the total sulfur on a monthly deposition-weighted average, but the sulfur concentrations in winter are generally only one-tenth those in summer, where very little sulfur dioxide in precipitation is found.

.cks, B. B., "An Evaluation of Precipitation Scavenging Rates of Background Aerosol," _J. Appl. Meteoro._, _17_, 161-165, 1978.

Concentrations of radon daughters in falling rain are used to derive precipitation scavenging rates of natural, background aerosols, with which the radon daughters are assumed to be associated. Scavenging rates ranging from 10^{-4} to 10^{-3} s^{-1} are deduced from comparisons of the observations with the predictions of a simple model of in-cloud scavenging processes. The observational data were obtained during a series of intensive storm investigations, conducted at Argonne National Laboratory during summer conditions.

Hill, F. B. and R. F. Adamowicz, "A Model for Rain Composition and the Washout of Sulfur Dioxide," _Atmos. Environ._, _11_, 912, 1977.

A model for the washout of sulfur dioxide from the atmosphere by rain was developed in which account was taken of mass transfer of SO_2 into well-mixed drops, of ionic equilibrium of sulfur compounds in solution, of oxidation of dissolved species to sulfate ion, and of presence in the rain of background strong acid or base.

Newman, L., "General Considerations on How Rainwater Must Obtain Sulfate Nitrate and Acid," presented before the Division of Environmental Chemistry, American Chemical Society, Honolulu, HI, April 1-6, 1979.

It is shown that rainwater must obtain an appreciable fraction of its sulfur and acidity by incorporation of sulfur dioxide and that the nitrogen and its acidity could come from either nitrogen dioxide or nitric acid. Inferences can be made that in-cloud processes must be important in this regard, and that the acidity of the nitrate and sulfate cannot come exclusively from aerosols.

directly proportional to the sulfate concentration of the air ingested into the cloud and inversely proportional to cloud water concentration. The removal of airborne sulfate by precipitation is forecast to be strongly dependent upon the mechanism of precipitation formation with convective precipitation scavenging a factor of 2 to 10 higher sulfate concentrations than cold, layered clouds.

Scott, B. C., "The Impact of the Proposed Atikoken Electric Generating Facility on the Wet Deposition of Sulfur in the Boundary Waters Canoe Area," Pacific Northwest Laboratory Report PNL-2675 (to appear as a contribution in an EPA impact document), 1978.

At precipitation pH values greater than 4.9, the net wet flux of sulfur emitted from the Atikoken facility is predicted to be determined primarily by the washout of SO_2. At pH values less than 4.4, sulfate wet removal is predicted to contribute the bulk of sulfur deposited on the ground.

Scott, B. C., "The Sulfur Budget Dilemma?", Pacific Northwest Laboratory Annual Report for 1978 (to be published), 1979.

Wet removal values of sulfur, nearly identical to those observed over the MAP3S region (i.e., 30% of emitted S removed in summer, 5% of emitted S removed in winter) can be theoretically computed if one considers the atmospheric convergence associated with storms and the age of the air mass being scavenged.

Scott, B. C. and M. T. Dana, "Wet Removal Rates for SO_2 Gas and SO_4 Aerosol," submitted for publication in Atmos. Environ., 1979.

Sulfate removal is computed by assuming the subcloud sulfate aerosol act as cloud condensation nuclei, and are removed by the accretion process. SO_2 removal is modeled as occurring by accretion of drops by falling snowflakes, or is treated as an equilibrium process for falling water drops. SO_4^- wet removal rates are predicted to be near 40% h^{-1}, while SO_2 removal is predicted to be near 2% h^{-1}.

Scott, B. C. and N. S. Laulainen, "On the Concentration of Sulfate in Precipitation," accepted for publication in J. Appl. Meteoro., 1979.

Data collected during snow storms in Muskegon, Michigan, suggest that existing sulfate aerosol was incorporated into cloud

aqueous phase oxidation of SO₂ was ... the observed sulfate concentrations.

nnon, J. D., "A Gaussian Moment-Conservation Diffusion Model," <u>J. Appl. Meteoro.</u>, in press, 1979.

A numerical model of diffusion, involving the approximate conservation of zero-th, first and second moments of pollutant mass, is calculated with the assumption of Gaussian subgrid-scale distributions. Simulations of pollutant transport in a two-dimensional wind field with constant angular velocity indicate that the extent of pseudo-diffusion is acceptably small for many modeling situations and that the technique is computationally efficient.

CHAPTER 11: WEATHER AND CLIMATE MODIFICATION

Ackerman, B., S. A. Changnon, Jr., G. Dzurisin, D. F. Gatz, R. C. Grosh, S. D. Hilberg, F. A. Huff, J. W. Mansell, H. T. Ochs, III, M. E. Peden, P. T. Schickendanz, R. G. Semonin, and J.L. Vogel, "Summary of METROMEX, Volume 2: Causes of Precipitation Anomalies," Bulletin 63, Illinois State Water Survey, Urbana, IL, 395 pp, 1978.

The relevant observations obtained during the 5-year program are described and synthesized to provide insight into the cause of altered urban weather.

Changnon, S. A., Jr., F. A. Huff, P. T. Schickedanz, and J.L. Vogel, "Summary of METROMEX, Volume I: Weather Anomalies and Impacts," Bulletin 62, Illinois State Water Survey, Urbana, IL, 260 pp, 1977.

Summarizes the identified and quantified urban-related weather anomalies in the St. Louis area and addresses the resulting effects on the socio-economic structure of the region.

Gatz, D. F., "Comment on 'Acid Precipitation in the Northeastern United States'," by C. V. Cogbill and G. E. Likens, <u>Water Resources Res.</u>, <u>12</u>(3), 569-570, 1976.

This comment questions the use of 500 mb trajectories in the Cogbill and Likens paper to trace the source of the acidity found in precipitation.

clouds. Aircraft, ground generators, and rockets have been used to release at least 13 different tracer materials. Most results claim nearly 100% removal to the ground and very complex mesoscale transport before deposition. However, this depends on background assessment, which generally has not been adequate.

Gatz, D. F., "Identification of Aerosol Sources in the St. Louis Area Using Factor Analysis," J. Appl. Meteoro., 17(5), 600-608, 1978.

This paper shows how filter sampling of ambient aerosol, followed by multi-element analysis of the filters and factor analysis of the results, can be used to identify sources. Widespread sources in the St. Louis area include soil dust and flyash, secondary sulfates, auto exhaust, and metals. Local sources detected include a titanium pigment plant and a secondary lead smelter.

Gatz, D. F., "A Test of the 'Pollution Increases Rain' Hypothesis at St. Louis," to be submitted to J. Appl. Meteoro., 1979.

Results from METROMEX suggest that rainfall is increased after a moving raincell intersects the urban plume. This paper tests the hypothesis that the aerosol component of the plume is the causative mechanism. The results show larger correlations than expected by chance between rainfall in certain areas and source strength of fine groups of urban aerosols. However, physical reasoning does not support an aerosol involvement in the urban rainfall anomaly.

Peden, M. E. and L. M. Skowron, "Ionic Stability of Precipitation Samples," Atmos. Environ., 12(12), 23-43, 1978.

This paper illustrates the problems of precipitation chemical analysis quality assurance as influenced by handling and storage methodologies. The results indicate changes in some ionic species of > 50% within a few days of a precipitation event emphasizing the need for care of sample handling and the adoption of standards to insure compatibility of results between various networks.

Semonin, R. G., B. Ackerman, D. F. Gatz, S. D. Hilberg, M. E. Peden, R. K. Stahlhut, and G. J. Stensland, "Study of Air Pollution Scavenging," Fifteenth Progress Report, Contract EY-76-5-02-1199, Illinois State Water Survey, Urbana, IL, 120 pp, 1977.

The report identifies three major topics of research including

aerosol chemistry section describes measurements distributions obtained in St. Louis, source identification of the major aerosol components, and their concentration. The precipitation chemistry interlaboratory analytical comparisons are presented in the second section with a discussion of trends in pH in central Illinois. The meteorology section describes the results from the St. Louis surface temperature and humidity network and the boundary layer airflow program.

monin, R. G., D. F. Gatz, M. E. Peden, and G. J. Stensland, "Study of Air Pollution Scavenging," Sixteenth Progress Report, Contract EY-67-5-02-1199 for U. S. Department of Energy, Illinois State Water Survey, Urbana, IL, 72 pp, 1978.

The relative spatial variability of precipitation chemical deposition is assessed and preliminary results are presented on the continuing research on detailed precipitation chemistry. The field efforts to measure wet deposition on a small time and space scale are described. The effects of precipitation sample handling and storage on the subsequent quality of the chemical analysis are given elucidating some of the serious problems involved.

Shannon, J. D. and M. L. Wesely, "Objective Re-evaluation of a Regional Turbidity Network," in Transactions of the Joint APCA/ASQC Conference on Quality Assurance in Environmental Measurements, in press, 1979.

An objective analysis originally applied to help select the sites for the MAP3S turbidity network was again applied to reevaluate the network locations based on the first year of observations. The new correlation structure function indicates a stronger southwest to northeast spread of increased turbidity than in the first analysis. The data are not as complete as desired, indicating the need to use other measures of haziness in a supplementary fashion.

Shannon, J. D., M. L. Wesely and P. J. Brady, "Objective Sensor Placement for Sampling Regional Turbidity," Atmos. Environ., 12, 937-943, 1978.

Objective sensor-placement techniques are applied to the process of selecting locations for a network of ten silicon photocells, to sample atmospheric turbidity in the MAP3S region. A suitable correlation structure function can be found for data oresently available from Volz sunphotometers, and sensor

the Summer Near Chicago," Atmos. Environ., 10, 981-987, 1976.

Atmospheric turbidity at a primarily-rural location in the Midwest causes a decrease in the direct-beam irradiance I at the surface of the earth, while the diffuse component D compensates under cloudless skies to offset 60-70% of the loss. The amount of haze is greater with southwest winds than with northwest winds. For the summertime conditions considered, haze tends to increase the effective earth albedo.

CHAPTER 12: NUMERICAL MODELING AND ANALYSIS

Davis, W. E., "The Effect of Using Time Averaged Precipitation for the Estimation of Wet Deposition in a Regional Scale Model," Proceedings of the Fourth Symposium on Turbulence, Diffusion and Air Pollution, American Meteorological Society, Boston, MA, 1979.

The results of this study showed that large differences can occur in estimating wet deposition through the use of monthly averages of precipitation versus shorter term averages. In general, the larger the washout ratio the larger the difference. A second method was tested using an on/off switch of seven hours of precipitation every 72 hours. This technique produced deposition results much closer to the values produced by hourly precipitation than those by the use of average precipitation for the periods studied. More work is necessary to test out this technique during summer months for convective rainfall.

A comparison of wet deposition from the single layer PNL model with an eight layer PNL model showed much less deposition occurring in the eight layer model. This difference was attributed to the calculation of wet deposition using a washout ratio a factor of ten smaller when saturation of the puff did not occur and rain was occurring.

Husain, L., P. E. Coffey, R. E. Meyers, and R. T. Cederwall, "Ozone Transport from Stratosphere to Troposphere," Geophys. Res. Letters, 4, 363-365, 1977.

[7]Be produced by the interaction of cosmic rays with oxygen and nitrogen, predominantly in the stratosphere, has been used to identify and measure stratospheric ozone at ground level. Simultaneous measurements at Whiteface Mountain, New York, in July 1975 show that the maximum [7]Be concentrations are

also important with respect to the upper boundary condition of air quality models.

Lee, H. N. and R. E. Meyers, "On the Time-Dependent Multi-Grid Numerical Technique," presented at the Second International Conference on Computational Mechanics, 26-28 March 1979, Austin, Texas.

   The multi-grid method which employs a sequence of nested grids in the solution process is a general numerical technique for solving continuous problems. Implementation of the multi-grid algorithm can result in higher accuracy and efficiency than methods with the fixed-grid size and fixed order of approximation; the specific tests of this are considered in the present study. An introduction to the implementation of the multi-grid method in the solution of a time-dependent partial differential equation is presented. Multi-grid solutions for the advection equation are compared with published results using the usual fixed-grid method.

MacCracken, M. C., "Simulation of Regional Precipitation Chemistry," in Proceedings of the Advisory Workshop to Identify Research Needs on the Formation of Acid Precipitation, August 22-25, 1978, Alta, Utah, Electric Power Research Institute, Palo Alto, CA, 1978 (also available as Lawrence Livermore Laboratory Report UCRL-81562).

   At present, capabilities for comprehensive modeling of regional patterns of air quality and precipitation chemistry are seriously deficient; however improvements are being made. Elementary calculations indicate that significant limitations in the understanding of sulfur and hydrogen ion budgets pose basic dilemmas that restrict progress in modeling. Well-designed and focused field and laboratory investigations are needed so that comprehensive modeling efforts can be carried through.

Meyers, R. E. and R. T. Cederwall, "Comments on The Mixing Height and Mass Balance of SO_2 in the Atmosphere Above Great Britain," Atmos. Environ., 10, 790-791, 1976.

   Comments were made concerning a published article by J. A. Garland and J. R. Branson. It was pointed out that in estimating the mean height of the SO_2 mixing layer, Garland and Branson had in fact calculated the mixing height of the mean SO_2 concentration profile rather than the mean mixing height of the concentration profiles. In addition, SO_2 data at one location

under rather restricted meteorological conditions were not an adequate basis for estimating the general residence time of SO_2 over Great Britain.

Meyers, R. E., R. T. Cederwall, L. I. Kleinman and S. E. Schwartz, "Long-Range Transport of Sulfur in the Eastern United States," in An Assessment of National Consequences of Increased Coal Utilization, Vol. 1 and 2, U. S. Department of Energy, Office of Technology Impacts, Washington, D. C., 1978.

A summary of extensive air quality analyses is presented as it relates to projected sulfur oxide air quality in the eastern U.S. associated with the increased use of coal under the National Energy Plan. Results of the analyses, coupled with population to give exposure estimates, are used elsewhere in the volumes to assess impacts on human health.

Meyers, R. E., R. T. Cederwall, J. A. Storch, L. I. Kleinman, "Modeling Sulfur Oxide Concentrations in the Eastern United States: Model Sensitivity, Verification and Applications," Proceedings of the Fourth Symposium on Atmospheric Turbulence, Diffusion and Air Quality, American Meteorological Society, Boston, MA, 673-676, 1979.

This paper briefly reports on results from the BNL long- and short-range transport model. The model (AIRSOX: Atmospheric Impact of Residual SO_x) calculates the transport, transformation and resulting pollutant concentrations for given SO_x emission inventories. Results from extensive sensitivity analyses are reported. Calculations for results in the United States are presented.

Meyers, R. E., C. Dopazo, R. Scott, and E. E. O'Brien, "Applications of Probability Densities and Intermittency to Random Processes in Environmental Chemistry and Hydrodynamics," in Advances in Environmental Science and Engineering, Gordon and Breach Publishers, 1979.

This article reviews the state-of-the-art of application of probability densities to hydrodynamics and chemistry problems.

Meyers, R. E., E. E. O'Brien and L. R. Scott, "Random Advection of Chemically Reacting Species," J. of Fluid Mechanics, 85, 233-240, 1978.

In the absence of molecular diffusion there exists a

undergoing advection alone. In two well-known limits the equation for the probability density of non-reacting scalars is linear and parabolic in physical space. In such cases it is shown that the equation for the probability density of reacting scalars is likewise linear and parabolic in physical space, although hyperbolic in concentration space. The general solution of such an equation is obtained and the particular case of a second order, decaying, single-species reaction is displayed.

Meyers, R. E. and E. N. Ziegler, "Statistical Correlation Between Ambient Sulfate Concentration and Sulfur Dioxide Concentration, Total Suspended Particulates, and Relative Humidity for 13 Eastern States," Environ. Science and Tech., 12, 302-309, 1978.

Daily ambient sulfate concentrations (C_2) measured in the 13 eastern states were related to SO_2 concentrations (C_1), particulate concentrations (C_p), percent relative humidity (H), temperature (T), and solar radiation (S). A semi-empirical Lagrangian box model and non-linear generation kinetics were used to develop simple relationships for sulfate with meteorological and chemical quantities. Laboratory results concerning the mechanism of sulfate formation were reviewed and discussed in relation to the atmospheric variables. At low temperature $(T < 50^{\circ}F)$, C_2 was correlated with C_1, C_p and H. At higher temperature $(T > 50^{\circ}F)$, higher correlation coefficients resulted when C_2 was related to C_p alone than when related to any other combination of variables tested.

O'Brien, E. E., "Stochastic Properties of Scalar Quantities Advected by a Non-Buoyant Plume," J. Fluid Mech., 89, 209-222, 1978.

A model probability density equation is obtained by approximating the convective and diffusive terms in a single-point density formulation of homogeneous turbulent scalar transport, with first-order reaction, in a plume. The equation, which includes the intermittency factor of the scalar field explicitly, is there shown to support similarity solutions under some constraining assumptions. Comparison of the similarity solutions with field measurements of conditioned concentrations shows that they can reproduce measurement regimes. On the basis of these asymptotic results a speculative modeling of the terms representing entrainment at the plume interface is proposed and a class of similarity solutions for the intermittency factor is obtained by numerical integration.

This report describes a sulfur oxide atmospheric pollution model that calculates trajectories using single-layer historical wind data as well as chemical transformation and deposition following discrete contaminant air masses. Vertical diffusion under constraints is calculated, but all horizontal dispersion is a function of trajectory variation. The ground-level air concentrations and deposition are calculated in a rectangular area comprising the northeastern United States and southeastern Canada. Calculations for a 29-day assessment period in April 1974 are presented along with a limited verification. Results for the studies were calculated using a source inventory comprising 61% of the anthropogenic SO_2 emissions. Using current model parameterizations, predicted concentration values are most sensitive to variations in dry deposition of SO_2, wet deposition of sulfate, and transformation of SO_2 to sulfate. Replacing the variable mixed-layer depth and variable stability features of the model with constant definitions of each results in increased ground-level concentration predictions for SO_2 and particularly for sulfate.

Shannon, J. D., "The Advanced Statistical Trajectory Regional Air Pollution Model," in Proceedings of the 4th Symposium on Turbulence, Diffusion, and Air Pollution, American Meteorological Society, Boston, 376-380, 1979.

An advanced statistical trajectory model of regional pollution dispersion has been applied to predict concentrations of sulfur pollutants and deposition patterns. Horizontal dispersion statistics are developed from the release of simulated tracers from each source, while vertical dispersion statistics are produced by numerical integration of the one-dimensional diffusion equation. The integration includes parameterizations of diurnal patterns of stability profiles, deposition velocities, transformation rates, and emission rates. Wet removal of total sulfur is assumed to be proportional to the half-power of the hourly precipitation. Simulations of sulfur pollution over the eastern United States and southern Canada are compared to available observations.

Sheih, C. M., "On the Relative Importance of Single-Particle and Relative Diffusion for Plume Dispersion," in Proceedings of the 5th Conference on Probability and Statistics in Atmospheric Sciences, American Meteorological Society, Boston, 265-268, 1977.

types of diffusion have to be included in calculations.

Sheih, C. M., "Application of Statistical Trajectory Model to the Simulation of Sulfur Pollution over Northeastern United States," *Atmos. Environ.*, 11, 173-178, 1977.

The long-term average plume from each pollutant source is approximated by a series of puffs in which the horizontal distribution of pollutant concentration is assumed to be Gaussian. The vertical distribution of material in each puff is computed from a numerical integration of two equations that describe the budgets of sulfur dioxide and sulfate. Pollutant sources corresponding to 53 major power plants in the northeastern United States are considered.

Sheih, C. M., "Mathematical Modeling of Particulate Thermal Coagulation and Transport Downstream of an Urban Area Source," *Atmos. Environ.*, 11, 1185-1190, 1977.

A finite-difference model incorporating the mechanisms of thermal coagulation and gravitational sedimentation in the equation of diffusion is used to predict the particulate size distribution from an urban area source. The predicted spectral shape simulates observations fairly well. The effect of gravitational sedimentation and coagulation is found to be negligible for particles in the range of 0.1-1μm. Consequently, the number spectrum should peak at this range in an equilibrium state.

Sheih, C. M., "A Puff-grid Model for Predicting Pollutant Transport Over an Urban Area," *J. Air Pollu. Control Assoc.*, 27, 784-785, 1977.

A scheme is proposed for improving spatial resolutions encountered in urban or regional-scale finite difference diffusion models. For example, the horizontal grid size of 1km used in urban models effectively dilutes the strength of a source of the order of 1 m diameter (a typical smoke stack) by a factor of 10^6. In order to address this problem, the present simulation treats the subgrid scale sources with a puff model. The pollutant in each puff is passed to a grid model after the puff has grown to a size comparable with the grid volume.

and Diffusion," <u>Appl. Meteoro.</u>, <u>17</u>, 140-147, 1978.

A scheme is developed to minimize the pseudo-diffusion that arises in numerical solutions of finite-difference equations of turbulent diffusion and transport. Lagrangian puffs are advected by the mean wind and puff boundaries are expanded or contracted by diffusive displacements, which are computed from the values of concentration, atmospheric turbulent diffusivity, and the gradient of pollutant concentration between adjacent grid volumes. The pollutant is then distributed back to surrounding Eulerian grid volumes, preserving the first and the second moments of the concentration distribution.

Sheih, C. M., "A Puff Pollutant Dispersion Model with Wind Shear and Dynamic Plume Rise," <u>Atmos. Environ.</u>, <u>12</u>, 1933-1938, 1978.

A puff diffusion model, that includes wind shear and dynamic plume rise has been developed for application under unsteady and non-uniform flow conditions. The plume from a continuous source is treated as a series of puffs emitted successively from the source. Each puff is represented by a set of six tracer particles, which define the size, shape and location of the puff. The locations of the particles are computed at each time step by taking into account advection, eddy diffusion, wind shear and entrainment of ambient air during plume rise.

Sheih, C. M. and G. D. Hess, "Temporal Sampling Requirements for Long-Term Atmospheric Pollutant Dispersion Studies," <u>J. Geophys. Res.</u>, <u>83</u>, 6259-6261, 1978.

A statistical sampling theory was used to compute the temporal sampling interval and the sampling duration required for statistical studies of long-term horizontal dispersion of pollutants. An analysis of the simulated trajectories according to season indicates that the minimum interval required for statistical independence of samples varies from a minimum value of 20 hours for winter to a maximum value of 49 hours for spring. The requirements for computing annual average pollutant concentrations are also discussed.

Sheih, C. M., G. D. Hess and B. B. Hicks, "Design of Network Experiments for Regional-Scale Atmospheric Pollutant Transport and Transformation," <u>Atmos. Environ.</u>, <u>12</u>, 1745-1753, 1978.

The design of regional scale air pollution sampling networks

transport, or to measure air quality experiments and evaluate the extent of air pollution. In the case of regional-scale tracer experiments a minimum of two lines of five surface stations are desirable. The spatial separation between the lines should be about 400 km, with the distances between stations being about 170 km for the upstream line and 200 km for the downstream line.

C. M., P. J. Mulhearn, E. F. Bradley and J. J. Finnigan, "Pollutant nsfer Across the Cavity Region Behind a Two-Dimensional Fence," os. Environ., 12, 2301-2308, 1978.

A simple mathematical expression for predicting pollutant concentration inside the cavity region downstream of a fence (or a two-dimensional mountain ridge) has been formulated and the associated wind tunnel simulation has been conducted. The pollutant concentration inside the cavity region is parameterized as a function of fence height, the horizontal dimension of the cavity region, the free-stream wind velocity and the free-stream pollutant concentration.

G. D., G. T. Wolff, P. J. Lioy, R. E. Meyers and R. T. Cederwall, rmation and Transport of Ozone in the Northeast Quadrant of the ted States," in Air Quality Meteorology and Atmospheric Ozone, TM STP 653, A. L. Morris and R. C. Barras, Eds., American Society Testing Materials, 445-457, 1978.

The very high concentrations of ozone measureed in Connecticut and elsewhere along the Northeast and Mid-Atlantic Coast were investigated through analysis of data from the entire 1976 elevated ozone season from 19 northeastern and mid-western states. National Weather Service meteorological data, and air parcel trajectories, for several high ozone episodes, the relationship between the movement of and circulation within a high pressure system across the northeast quadrant of the United States and the buildup of ozone concentrations was clearly demonstrated. Air parcel trajectory analysis, coupled with source density information, was utilized for several well-defined episodes in 1976 to show that ozone measured at various locations throughout the study area is partially generated locally and partially transported from substantial distances.

G. T., P. J. Lioy, G. D. Wight, R. E. Meyers, and R. T. Cederwall, n Investigation of Long-Range Transport of Ozone Across the dwestern and Eastern United States," Atmos. Environ., 11, 797-802,

patterns and comparing them with synoptic meteorological features and air parcel trajectories for a 2-week period in April 1976. This period was characterized by the presence of a large high pressure system which produced widespread ozone concentrations in excess of .08 ppm and extremely high maximum temperatures for April. Movement of areas of high ozone concentrations correspond to the movement of the high pressure system; the long-range transport was supported by trajectory analyses. Daily visibility data suggested that areas of low visibility generally coincide with areas of high ozone under certain conditions.

Yamada, T., "A Numerical Experiment of Pollutant Dispersion in a Horizontally Homogeneous Atmospheric Boundary Layer," Atmos. Environ., 11, 1015-1024, 1977.

A simplified turbulent closure model is proposed and utilized for simulation of the three-dimensional dispersion of pollutants in the lower atmosphere. A three-dimensional mass conservation equation for a chemically inert pollutant is integrated numerically, with use of mean value and turbulence fields from the numerical results of the first part. As expected, the results indicate large differences in the pollutant profiles of pollutant concentration between days and nights, due to changes in atmospheric stability. The values of the surface pollutant concentration are significantly reduced, especially at night when the emissions are assumed to be from a 200 m stack.

Yamada, T., "A Three-dimensional Numerical Study of Complex Atmospheric Circulations Produced by Terrain," in Proceedings of the Conference on Sierra Nevada Meteorology, American Meteorological Society, Boston, 61-67, 1978.

Numerical simulations are performed in order to investigate complex atmospheric circulations produced by terrain. The model used is a second-moment turbulence closure model. As a first step toward including more complex and realistic terrain, numerical simulations of the airflow over single and multiple Gaussian-shaped mountains are studied. Preliminary results for the case of a single, 500 m high Gaussian mountain indicate that horizontal wind speed in the lee of the mountain may increase, under some conditions, by 100% over that at the inflow boundary. Divergence and convergence of the horizontal wind field result in vertical motion through the continuity equation. A maximum

is computed over the mountain, bringing down warmer (in terms of the potential temperature) and drier air.

Yamada, T., "A Numerical Study of the Effects of Complex Terrain on Dynamics of Airflow and Pollutant Dispersion," in *Proceedings of the 4th Symposium on Turbulence, Diffusion, and Air Pollution*, American Meteorological Society, Boston, 213-216, 1979.

A three-dimensional, second-order turbulence closure model has been developed to investigate atmospheric perturbations and pollutant dispersion over single and multiple mountains. Preliminary analyses of the results indicate that concentrations are minimal over the lee of the mountain mainly due to the subsidence of clean air and to the "split" of horizontal winds around the mountain. Turbulent mixing becomes important when the atmosphere is unstable due to the heating from the surface. Fumigation under unstable conditions leads to concentrations downwind of the mountain that are higher than those under stable conditions.

CHAPTER 13: SPECIAL ACTIVITIES

Benkovitz, C. M., "Facilitating Data Exchange Within ERDA," presented at the VIM26 Conference, Minneapolis, Minn., April 1977, Brookhaven National Laboratory Report BNL-22595, April 1977.

This paper presents the background and development of a proposed standard for the interchange of data via magnetic tape by a working group of representatives of seven ERDA (now DOE) National Laboratories. The basic standard was presented to the ANSI X3L5 subcommittee and after minor revisions is now known as the Proposed American National Standard Specifications for an Information Exchange Data Descriptive File.

Benkovitz, C. M. and R. A. Wiley, "Users' Guide for the Implementation of Level One of the Proposed American National Standard Specifications for an Information Exchange Data Description File on Control Data 6000/7000 Series Computers," BNL-23393, Brookhaven National Laboratory, Upton, NY/LA-6940-MS, Los Alamos Scientific Laboratory, Los Alamos, NM, September 1977.

This document defines the user interface to an implementation of level 1 of the proposed ANSI standard on CDC 6000

(2 issues), 1977 (4 issues), 1978 (4 issues).

The MAP3S newsletter is issued quarterly to report plans and progress related to study of sulfur pollution in the northeastern United States. More than 500 copies of the last issue of the newsletter were distributed to interested scientists, government officials, and interested groups.